



EUROPEAN CONFERENCE ON GAS HYDRATE



June 13-16, 2022
Lyon, France

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SPONSORS



Monday 13th

8h-9h : Registration, Welcome Coffee

9h-9h15 : Opening session

9h15-10h35 : ORAL, 4 presentations Session 1

- *Could mixed carbon dioxide and propane hydrates form structure I?* Baptiste Bouillot, Saheb Maghsoodloo Babakhani, Charlene Guimpier, Vivian Nassif, Jean-Michel Herri, Arnaud Desmedt
- *Hydrate-like Order Propagation Promotes Nucleation of CH₄ Hydrate in the Presence of Ice: A Molecular Dynamics Study* ; Dalip Kumar, Shiang-Tai Lin, David Tai-Wei Wu
- *Stability and metastability of clathrates hydrates with DFT simulations* ; Ludovic Martin-Gondre, Arnaud Desmedt, Cyrielle Métais
- *Utilization of machine learning on FT-ICR MS spectra for improved understanding and prediction of the properties of hydrate-active components* ; Elise Lunde Gjelsvik, Martin Fossen, Anders Brunsvik, Sylvia Weging, Kristin Tøndel

10h35-11h : POSTERS (all sessions) and coffee break

11h-12h : ORAL, 3 presentations Session 1

- *Water content measurements in liquid Ethane in equilibrium with water or hydrates: new measurements and literature data evaluation* ; abdulla alassi
- *Water Content of Carbon Dioxide in Equilibrium with Hydrates* ; Valderio de Oliveira Cavalcanti Filho, Antonin Chapoy, Rod Burgass
- *Yield characteristics of hydrate-sand slurry* ; Shunkang Fu, Shangfei SONG, Bohui SHI, Xu Duan, Qingyun Liao, Jing GONG

Lunch (Brasserie Georges)

14h20-16h : ORAL, 4 presentations Session 1

- *A new high pressure method for successive accumulation of hydrate active components* ; Martin Fossen, Anders Brunsvik, Elise Lunde Gjelsvik, Marita Wolden, Are Lund, Kristin Tøndel
- *Advances in Environmental Profile for Anti-Agglomerant Low Dosage Hydrate Inhibitors (AA-LDHIs)* ; Jeremy Bartels, Rebecca Lucente-Schultz
- *Influence of thermodynamic inhibitors in interfacial rheology of cyclopentane hydrates* ; Monica Naccache, Marina Bandeira, Gustavo Sandoval, Paulo de Souza Mendes, Leandro Valim, Adriana Teixeira
- *Phenomenological Analysis of Hydrate Deposition in Non-Emulsified Systems* ; Daniela Marques, Celina Kakitani Ofuchi, Carlos Bassani, Moisés Marcelino Neto, Amadeu Sum, Rigoberto Morales

16h-17h : POSTERS (all sessions) and coffee break

17h-18h20 : ORAL, 4 presentations Session 5

- *Clathrate hydrates FTIR spectroscopy to understand cometary ices* : Natalia Esteves Lopez, Aurélie Guilbert-Lepoutre, Stephane Coussan, Arnaud Desmedt
- *From clathrate to clathrite in other ocean worlds* : Ana de Dios Cubillas , Olga Prieto-Ballesteros
- *Clathrate substitution leading to gas generation in Titan subsurface* : Shunsuke Nozaki, Yasuhito Sekine, Yunfeng Liang, Wuge Cui, Hidenori Genda, Takeshi Tsuji, Yoshihiro Masuda
- *Exploring stability and new structures of H₂, CH₄ - hydrates under planetary conditions* : Bove Livia Eleonora

Tuesday 14th

8h30-9h : Welcome Coffee

9h-10h : ORAL, 3 presentations Session 3

Special session on the Geomechanical aspects of gas hydrate-bearing sediments co-convened by Dr. Assaf Klar

- *Cohesion in Methane Hydrate-Bearing Soil; To Be or Not To Be?*, Shmulik Pinkert
- *Mechanical behaviour and microstructure of methane hydrate-bearing sandy sediment*, Thi Xiu Le, Michel Bornert, Ross Brown, Patrick Aïmedieu, Daniel Broseta, Baptiste Chabot, Andrew King and Anh Minh Tang
- *Micromechanical Investigations of Gas Hydrate Bearing Sediments*, Eitan Cohen and Assaf Klar

10h-11h : POSTERS (all sessions) and coffee break

11h-12h : ORAL, 3 presentations Session 3

- *Gas selectivity of the thermogenic-like gas hydrates: experimental and modelling*, Olivia Fandino, Charlène Guimpier, Arnaud Desmedt and Livio Ruffine
- *Macroscopic Insight into the Hydrate Decomposition Kinetics below Freezing Point of Water*, Meng Shi, John M. Woodley and Nicolas von Solms
- *BSRs levels in the west Antarctic Peninsula margin: an inventory of seismic indicators of marine gas hydrates*, Ricardo León, Roger Urgeles and Lara Pérez

Lunch (on site, BBQ Party, "pétanque" competition)

14h-15h40 : ORAL, 4 presentations Session 3

Special session on the Black Sea Hydrate Systems co-convened by Dr. Ewa Burwicz-Galerne

- *Basin-scale gas hydrate estimates in the Black Sea derived from 3D modelling*, Ewa Burwicz-Galerne, Matthias Haeckel and Klaus Wallmann
- *Gas-hydrate reservoir characterisation through joint interpretation of geophysical data in the Danube deep-sea fan, Black Sea*, Jörg Bialas, Ingo Klauke, Laura Gassner, Anke Dannowski, Sebastian Hölz, Gerald Klein, Michael Riedel, Katrin Schwalenberg and Erik Spangenberg
- *Simulating multiple BSRs in the dynamic gas hydrate stability zone of the Danube paleo-delta, Black Sea*, Shubhangi Gupta, Christian Deusner and Matthias Haeckel
- *Laboratory to field scale investigations of methane hydrate formation in clay-rich sediments: towards a better understanding of the Black Sea natural gas hydrate system*, Constant Agnissan, Charlène Guimpier, Sandrine Chéron, Marco Terzariol, Olivia Fandino, Vincent Riboulot, Arnaud Desmedt and Livio Ruffine

15h40-16h40 : POSTERS (all sessions) and coffee break

16h40-18h : ORAL, 4 presentations Session 3

- *CO₂ storage in depleted reservoir: a methodology to assess hydrates risk in the near wellbore area*, Anne Sinquin, Marc Fleury, Thibaud Chevalier, Matthieu Mascle, Souhail Youssef, Nicolas Gland, Audrey Estublier, Tuyêt-Hang Le Goff, Frédéric Lagarde and Luc Pauget
- *Demonstrating CO₂ hydrate stability in oceanic sediments on lab scale to promote CO₂ sequestration*, M Fahed Qureshi, Vikas Dhamu, Adam Usadi, Timothy A Barckholtz, mhadeshwar Ashish b and Praveen Linga
- *Hydrate Formation in Aqueous Solutions Undersaturated with CO₂*, Rod Burgass, Antonin Chapoy, Askvik Kjell, Neeraas Bengt Olav and Li Xiaoyun
- *Modeling CO₂ solubility in DESs using Cubic Plus Association and Peng-Robinson Equations of State*, Fernanda Pelaquim, Débora Nascimento, Raphaela Bittencourt, Antonio Barbosa Neto, Irede Dalmolin and Mariana Costa

Wednesday 15th

8h30-9h : Welcome Coffee

9h-10h : ORAL, 3 presentations Session 2

- *Comparative study of the formation, the stability and the growth of methane hydrates in free, confined and ultra-confined organic environments by molecular modelling*, Ababakari Oumarou Ali and Patrice Bordat, France
- *Pre-screening of Protic Ionic Liquids as Hydrate Inhibitors with COSMO-RS*, Costa do Nascimento, et. al., Brazil;
- *CFD-PBM simulation of hydrate growth and agglomeration in a high-pressure cell*, Duan, et.al., China/Norway

10h-11h : POSTERS (all sessions) and coffee break

11h-12h : ORAL, 3 presentations Session 2

- *Multi-scale characterization of gas hydrates formed in the presence of antiagglomerant additive*, ABDALLAH, et. Al, France
- *Hydrate structural dependency of natural KHIs present in crudes compared to commercial KHI additives*, Lesage et.al., United Kingdom
- *Hydrate management by pore-sealing in oil-continuous systems*, Bassani et al. Brazil

Lunch (on site, Food Truck, "pétanque" competition)

14h-15h40 : ORAL, 5 presentations Session 2

- *Real Time Prediction of Dynamic Hydrate Deposition Trend Using PCA and Recurrent Neural Network with Iterative Transfer Learning*, Lee, et.al, Korea;
- *Mechanisms of hydrate blockage in oil-water dispersions based on flow loop experiments*, Almeida, et. al., France
- *Experimental study about the Horizontal Three-Phase Solid-LiquidGas Slug Flow with Hydrate-Like Particles*, Cavalli, et.al, Brazil;
- *Experimental Observations of Hydrate Deposition for Hydrate Management in Gas Filled Wellhead*, Lee, et.al., USA;
- *Practical decisions regarding reservoir hydrate risk mitigation in pre-salt projects*, Pinho, et.al, Brazil;

15h40-16h40 : POSTERS (all sessions) and coffee break

16h40-18h : ORAL, 4 presentations Session 4

- *Rheological and thermal study of mixed CP + CO₂ hydrate slurries for refrigeration applications* ; Nada Cham
- *Study on tetra-n-butylammonium bromide hydrate formation kinetics for cold storage and transport* ; Hyunho Kim, Junjie Zheng, Ponnivalavan Babu, Praveen Linga
- *Use of reverse micelles to enhance the formation of clathrate hydrates of hydrogen* ; Michele Ciulla, Valentino Canale, Nadia Barbacane, Rafal Damian Wolicki, Pietro Di Profio
- *How ionic defects play a role on the super-protonic conductivity of strong acid hydrates* ; Sophie Espert, Fabrice Mauvy, Brice Kauffmann, Daniel Sanchez-Portal, Arnaud Desmedt

18h-19h : on site, free time

19h-23h : Gala Diner on cruise boat (departure on site)

Thursday 16th

8h30-9h : Welcome Coffee

9h-10h : ORAL, 3 presentations Session 4

- *Formation and Growth of CO₂ and THF Hydrates in the presence of amino acid, amino acid derivatives and amino acid-based ionic liquids* ; Mario Soromenho, Anastasiia Keba, Jose Esperanca, Mohammad Tari
- *Impact of salt (NaCl) concentration on water recovery with CO₂ hydrates evidenced by in-situ Raman Spectroscopy* ; Sadain Zafar, Claire PIRIM, Bertrand CHAZALLON
- *Experimental heat transfer measurement applied to CO₂ hydrate formation kinetic study*; Véronique OSSWALD, Pascal CLAIN, Didier DALMAZZONE, Anthony DELAHAYE, Laurence FOURNAISON

10h-11h : POSTERS (all sessions) and coffee break and **BEST POSTER PRICE**

11h-12h : ORAL, 3 presentations Session 4

- *Phase Equilibrium for Sea/Waste water treatment and carbon storage with clathrate hydrates* ; Angsar Serikkali, Hieu Ngo Van, Trung-Kien Pham, Quang Duyen Le, jerome douzet, Jean-Michel Herri, Baptiste Bouillot
- *Probing selectivity and capture process in carbon dioxide-based gas hydrate: investigation by Raman spectroscopy* ; Carla Thais Rodriguez, Sadain Zafar, Ludovic Legoix, Valentino Canale, Michele Ciulla, Pietro Di Profio, Claire PIRIM, Bertrand CHAZALLON
- *Methane recovery and carbon dioxide disposal in natural gas hydrate reservoirs: experimental results of an italian research project* ; Federico Rossi, Beatrice Castellani, Alberto Maria Gambelli, Andrea Nicolini, Mirko Filipponi, Giorgio Minelli

12h30 : BEST ORAL PRICE

Lunch (on site or take away lunch boxes)

POSTERS

Session 1: Fundamentals

- A Critical Assessment of Gas Hydrates Phase Equilibria Predictions for Inhibited Systems with Salts and Organic Inhibitors ; Amadeu Sum
- A Novel Method for the Determination of the Hydrate Induction Time through Temperature Steps ; Rafal Damian Wolicki, Valentino Canale, Michele Ciulla, Nadia Barbacane, Pietro Di Profio
- Comparison of different viscosity models for two-phase liquids on the example of the oil-dased ice slurry ; Pavel G. Struchalin, Vegar Hovdenakk Øye, Boris V. Balakin
- Discovering Hidden Structures of Clathrate Hydrates ; Amadeu Sum, Yong Chen
- Effect of Host Framework on The Phase Behaviour and Nucleation of CO₂ Hydrates: Isotopic Effects ; Mario Soromenho, Jose Esperanca, Mohammad Tariq
- Energetics of mixed carbon dioxide and methane hydrate clathrates ; J. Manuel Recio, Álvaro Lobato, Alberto Otero-de-la-Roza, Fernando Izquierdo-Ruiz, Eduardo de Oliveira Gomes
- Equilibrium properties and phase behaviour of carbon dioxide hydrate from Monte Carlo simulations in the Gibbs ensemble with machine learning assisted analysis ; Paul Brumby
- Hydrate Deposition Characterization using Electrical Impedance Sensor in a Rock-Flow-Cell ; cesar ofuchi, Eduardo Nunes dos Santos, Celina Kakitani, Marco José Da Silva, Rigoberto Eleazar Melgarejo Morales
- Influence of parameters on ethane gas hydrate formation ; Monica Naccache, Ana Rebello, Gustavo Sandoval, Paulo de Souza Mendes, Leandro Valim, Adriana Teixeira
- Isopropanol : A hydrate promoter or inhibitor ? Experimental and thermodynamics structural analysis under different concentrations ; Moisés Marcelino Neto, Luiz Fernando Santos Vasconcelos, Kalwey L. Peniche, Giovanni T. Caldas, João V. M. Rocha, Thales Henrique Sirino, Rigoberto E. M. Morales
- Microscale investigation on methane hydrate formation kinetics: influence of sedimentary environment and NaCl ; Charlene Guimpier, Constant Agnissan, Vivian Nassif, Thomas Hansen, Livio Ruffine, Arnaud Desmedt
- Multiple Hydrate Structure Formation in Natural Gas Systems: Experimental Measurements and Modelling ; Ross Anderson, Antonin Chapoy, Rod Burgass, Bahman Tohidi
- Optimization of the SCC-DFTB potential to model aqueous systems : from liquid water to gas hydrates ; Nicolas Cinq, Jérôme Cuny, Aude Simon
- Paired KHI-MEG for synergistic inhibition of methane hydrate reformation ; Jinhao Sui, Bohui Shi, Xia Lou, Xu Duan, Shunkang Fu, Yumo Zhu, Shangfei Song, Haihao Wu, Jing Gong
- Surface Induced CO₂ Hydrate Nucleation and Growth ; Anastasiia Keba, Mario Soromenho, Jose Esperanca, Mohammad Tariq

Session 2: Crystallisation and flow modelling

- A Gibbs free energy model of phase equilibrium including gas hydrates ; Giorgia De Guido, Paolo Stringari, Marco Campestrini, Laura Pellegrini
- A method for quantitatively evaluating hydrate blockage risk in water-in-oil emulsion flow ; Xu DUAN, Shangfei Song, Boris Balakin, Bohui Shi, Jing Gong
- Air - Water Flow in a Rock&Roll Ring Flow Loop: Visualization and Modeling ; Madina Naukanova, Jérôme Douzet, Gianluca Lavallo, Ana Cameirao, Jean-Michel Herri
- Ethanol substitution by MEG as hydrate inhibitor on gas lines ; Tiago Perovano
- Functionalized Nanoparticles as Recyclable Hydrate Slurry Dispersants ; Amadeu Sum, Ning Wu, Yuanxing Zhang
- Study of Hydrate/Waxes Deposit's in Presence of AA-LDHI ; Anne SINQUIN, Brigitte BETRO, Emilie ABADIE, Nicolas LESAGE, Annie FIDEL-DUFOUR
- Water-Alternating-Gas (WAG) Subsea Injection Manifold: comissioning and operation experience ; Tatiana Metzger, Alexandre Cordeiro, Felipe Fleming, Fernando Arraes, Leonardo Carbone, Leonardo Guedes, Lilia Bukahi, Pedro Nogueira, Sergio Kazuo, Tatiana Pitchon

POSTERS

Session 3: Dynamics of Natural Systems and Carbon Storage

- Characteristics and morphology of CH₄/CO₂/N₂ mixed hydrates using multistep depressurization after hydrate swapping ; Qian OUYANG, Jyoti Shanker Pandey, Nicolas von Solms
- Characterization of free and sediment-trapped CO₂ and CH₄ gas hydrates by Raman and SEM measurements ; Rita Giovannetti, Andrea Rossi, Marco Minicucci, Michele Ciulla, Rafal Damian Wolicki, Valentino Canale, Pietro Di Profio
- Clathrate Hydrates for the Separation of CO₂ and CH₄ from Biogas: Study of Potential Kinetic Promoters ; Nadia Barbacane, Valentino Canale, Bertrand CHAZALLON, Michele Ciulla, Pietro Di Profio, Claire PIRIM, Rafal Damian Wolicki
- Formation of Gas Hydrates: the effect of the main natural parameters ; Beatrice Castellani, Rita Giovannetti, Alberto Maria Gambelli, Andrea Rossi, Federico Rossi
- MHBS Geomechanical Studies: Maintaining Experimental Consistency ; Ilior rake, Shmulik Pinkert
- Modeling the time-dependent dissolution of Gas Hydrates in the South Shetland Islands, Antarctica ; Doğa Düşünür Doğan, Neslihan Ocakoğlu Gökaşan, Umberta Tinivella, Michela Giustiniani, Selvican Türkdöğän, Sinan Arik, Zehra Altan
- Modelling of the phases of burial-driven gas hydrate and methane gas re-cycling ; Christopher Schmidt, Shubhangi Gupta, Ewa Burwicz-Galerie, Klaus Wallmann, Ebbe H. Hartz, Lars Rüpke
- On the existence of bifurcation manifolds in dynamical models of burial-driven gas hydrate recycling ; Shubhangi Gupta, Ewa Burwicz, Christopher Schmidt, Lars Rüpke
- Potential safe geological storage of CO₂ as mixed gas hydrates along the European continental margins ; Andre Burnol, Ricardo Leon Buendia
- Prediction of gas solubility in Deep Eutectic Solvents using COSMO-RS as a tool ; Fernanda Pelaquim, Débora Nascimento, Sérgio Villas-Boas, Pedro Carvalho, Antonio Barbosa Neto, Ireda Dalmolin, Mariana Costa
- Seafloor methane emissions in the Western Black Sea basin; Ewa Burwicz-Galerie, Rohit Samant
- Slope instabilities and gas hydrate dissociation in the western Black Sea since the last glacial maximum ; Maud Fabre, Lies Loncke, Vincent Riboulot, Nabil Sultan, Stephan Ker
- The case study of Electrical field simulating model with the production of Natural Gas hydrate in South China Sea ; Yuan Li, Hailong Lu, Evert Slob

Session 4: Hydrate based and energy efficient technologies

- A critical review of testing techniques for evaluating the performance of Kinetic Hydrate Inhibitors ; Bahman Tohidi, Bahram GHANBARI
- A thermodynamic and kinetic study on the mixed H₂/Dioxane sII hydrate for hydrogen storage ; Ye Zhang, Huanzhi Xu, Praveen Linga
- Combined Influence of Hydrate Structure and Corrosion Inhibitor on KHI Performance in Natural Gas Condensate Systems ; Ross Anderson, Annie Fidel-Dufour, Emilie Abadie, Nicolas Lesage, Bahman Tohidi
- Decomposition studies of CO₂-CH₄ hydrate depressurization process using molecular dynamic simulations ; Yunchao LI, Shangfei SONG, Xu DUAN, Qingyun LIAO, Bohui SHI, Jing GONG
- Effect of Gas Composition on Hydrate Growth Rate and Agglomeration Tendency ; Ross Anderson, Morteza Aminnaji, Bahman Tohidi
- Experimental heat transfer measurement applied to CO₂ hydrate formation kinetic study ; Véronique Osswald, Pascal Clain, Didier Dalmazzone, Anthony Delahaye, Laurence Fournaison
- High-efficiency Hydrogen storage by clathrate Hydrates; Federico Rossi, Beatrice Castellani, Alberto Maria Gambelli, Andrea Nicolini, Mirko Filipponi
- Hydrogen-rich Natural gas Hydrates Formation Kinetics ; Jyoti Shanker Pandey, Jesper Lundtoft Hansen, Nicolas von Solms
- Multiple Recovery and Re-use of Commercial Kinetic Hydrate Inhibitors from Produced Water and Rich Glycol ; Tore Larsen, Houra Mozaffar, Chris Henderson, Salim Deshmukh, Ross Anderson, Mohsen Hoopanah, Bahman Tohidi, Emilie Abadie, Vanessa Richon, Mark Charlesworth

Session 5 : Hydrates and Astrophysics

- Dielectric properties of CO₂ clathrate for the Jovian system exploration : Oscar Ercilla Herrero, Javier Sanchez-Benitez, Victoria Muñoz-Iglesias, Olga Prieto-Ballesteros
- Grand Canonical Monte Carlo Simulations for modeling gas trapping in Clathrate Hydrates : Sylvain Picaud, Julien Joliat, Antoine Patt
- Role of gas hydrate in the thermo-chemical evolution of Enceladus and Europa and potential detection by future space missions : Gabriel TOBIE, Erwan Lemenn, Benoit Seignovert, Olivier Bollengier, Stéphane, Lemouélic, Christophe Sotin

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Multi-scale characterization of gas hydrates formed in the presence of anti-agglomerant additive

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Hydrate management remains a major concern in Oil and Gas industries. The use of Low Dosage Inhibitor Hydrate (LDHI) is more and more used to mitigate hydrate issue instead of Thermodynamic Hydrate Inhibitor. When the oil and gas is produced in hydrate zones, anti-agglomerants (AA) additives is one type of LDHI which can be injected to prevent the agglomeration of the hydrates formed and to ensure their transfer in the pipeline without the risk of deposit or production shutdown. Investigating the impact of the anti-agglomerants additives on the size of the hydrates formed, their shape and their dispersion in the various phases constitute fundamental information required for future developments. In this issue, gas hydrates formed with various AA additives are studied by combining Raman microspectroscopy, X-ray micro-tomography and PV analysis. An original methodology has been developed to carry out the microtomography under controlled PT environment. The gas hydrates are formed at a constant pressure of 70 bar, by applying a constant cooling rate of 4 °C/h for 7 hours under a constant stirring rate of 500 rpm. The system is composed of Ketrul[®]211 phase (petroleum cut representing a condensate), a CH₄/C₃H₈ 92/8 % mol. gas and salted water (5 g/L NaCl) and 1 % wt. (regarding water) anti-agglomerant additive. The water cut is constant at 30 % vol. In addition to the in-situ imaging of the hydrate slurries and to the spectroscopic characterization of the various phases (water / condensate / gas), the structure, the cage occupancy, and the 3D distribution of the hydrate's grains (> 10 micrometers) have been investigated. This set of data yield a multi-scale characterization of the hydrate slurries formed with AA additives. The transfer procedure (reactors/hydrate cell) is successful. By using the microtomography, a sufficient contrast is obtained at 45 keV between water, Ketrul[®]211, air and PEEK. Through the RAMAN spectroscopy, several acquisitions for the additives, brine and Ketrul[®]211 phases are achieved. At the optimal wavelength 785 nm, gas hydrate characterization in the presence of anti-agglomerants additives can be performed without fluorescence restrictions.

Keywords : Gas hydrate, AA additives, multi-scale characterization, RAMAN spectroscopy, X-Ray micro Computed Tomography.

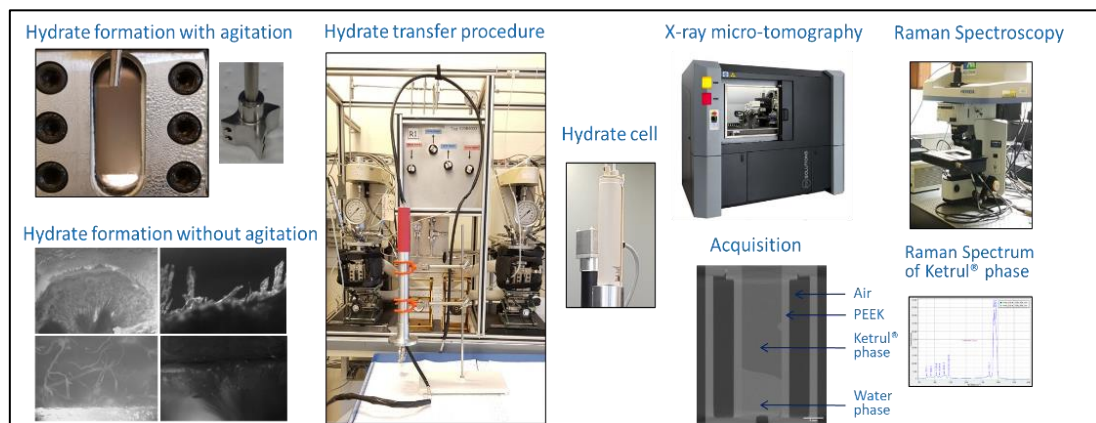


Figure 1 : Hydrate formation, transfer procedure, hydrate cell and acquisitions by X-ray microtomography and Raman spectroscopy.

Laboratory to field scale investigations of methane hydrate formation in clay-rich sediments: towards a better understanding of the Black Sea natural gas hydrate system

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The Black Sea, considered as one of the most isolated and methane-rich water body in the world¹, has been the object of scientific campaigns for several decades and host important accumulations of gas hydrates²⁻⁴. These hydrates accumulate in clay-rich sediments (~60% clay) of various types and depth-variable proportion⁵, which have a significant impact on their formation mechanisms at their habits. During the scientific cruises Ghass (2015) and Ghass2 (2021), hydrate specimens have been sampled in the Romanian sector of the Black Sea. In order to better understand the formation process of these hydrates, in particular the role of the sediment mineralogy, laboratory experiments on methane hydrate formation in different mixtures of sand, illite and montmorillonite, coupled with natural sample characterization have been performed. Visual inspections allowing to describe in details the hydrates distribution were completed by Raman micro-spectroscopy to study their gas storage capacity in relation with the sediment used. Physico-chemical and geochemical analyses were also carried out on hydrate-bearing samples recovered during the Ghass2 cruise. This work presents the macro and microscale differences and similarities between natural and synthetic specimens to get insights into the process governing the accumulation of hydrates within the Black Sea sediment.

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Multiple Hydrate Structure Formation in Natural Gas Systems: Experimental Measurements and Modelling

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While extensive experimental data and predictive modelling capabilities now exist with respect to incipient clathrate hydrate phase boundaries for single to multi-component natural gases, including complex systems involving liquid hydrocarbons, salts and thermodynamic inhibitors, phase behaviour within hydrate regions is far less well constrained, even though this is of great importance to both natural and industrial hydrate environments.

In many real-world situations, hydrate formation may take place far inside the phase boundary. Under such conditions, multiple stable/metastable clathrate phases may nucleate, grow, dissociate and/or undergo direct solid-solid transitions as systems tend to equilibrium.

In related works, it is described how such multiple structure formation processes are apparently closely linked to hydrate agglomeration / plugging tendency, natural slurry transportability, and LDHI (AA and KHI) performance. The same processes can likewise be expected in sediment-hosted gas hydrate systems, e.g. during gas production or CO₂ injection. For example, recent laboratory studies have shown clear evidence for multi-hydrate phase formation and solid-solid transitions during simulated flue gas sequestration in permafrost sediments.

Here, we present constant volume isochoric equilibrium PVT (pressure-volume-temperature) data for several natural gas systems that show the sequential formation of multiple hydrate phases/structures at equilibrium as subcooling / hydrate fraction increases. Depending on the initial PT conditions of hydrate growth, persistent structural hysteresis can also be observed, resulting in more than one (metastable?) equilibrium state. PVT data are supported by QCM (quartz crystal microbalance) studies that provide evidence for solid phases undergoing crystallographic / structural changes at higher subcoolings, including in single guest gas systems such as methane.

With the aim of better understanding the processes involved, an in-house thermodynamic model – which uses the CPA equation of state for fluid phases and the solid solution theory of van der Waals and Platteeuw for hydrate phases – has been used to predict observed behaviour, including the phase boundaries and fractions of structures present. Predictions agree well with experimental data, and support the sequential growth (as temperature is reduced) of a series of hydrate phases typically beginning with propane/butane stabilised (large cavity) s-II, followed by ethane stabilised (large cavity) s-II then s-I, before final methane-dominated s-I. At equilibrium, behaviour is ultimately driven by gas fractionation, although as noted, significant structural hysteresis and metastable phases can form depending on initial growth PT conditions, including a metastable s-II methane hydrate.

In addition to equilibrium predictions, boundaries for non-equilibrium incipient hydrate formation conditions are also predicted. These delineate the PT conditions where different hydrate structures can grow at subcooling even if they may not be the most thermodynamically stable phase, as observed in experimental studies. Such predictions are particularly important for flow assurance applications where hydrate growth may initiate at high subcoolings, e.g. in the case of KHI failure or following shut-in, cool-down and restart.

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Combined Influence of Hydrate Structure and Corrosion Inhibitor on KHI Performance in Natural Gas Condensate Systems

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Kinetic hydrate inhibitors (KHIs) are now well established as an effective technology for gas hydrate control in the oil & gas industry. They can offer significant CAPEX/OPEX advantages when compared with traditional thermodynamic inhibitors (e.g. methanol, glycols), in addition to helping significantly reduce the carbon footprint of conventional production operations. Historically, KHIs were tested by means of nucleation induction/hold time measurements, although in recent years the focus has turned to more robust crystal growth inhibition (CGI) approaches, which evaluate chemistries under worst-case scenario 'hydrate present' conditions.

It has been appreciated for some time that hydrate structure is important to KHI performance, with leaner s-I forming natural gases (NGs, mainly methane, with limited heavier hydrate formers) typically presenting more of a challenge than richer (in ethane, propane, butane) s-II dominated mixtures. CGI studies have facilitated a better understanding of the processes involved, and, for example, point to KHI 'failure' in s-II NGs often apparently being the result of an inability to inhibit s-I at higher subcoolings.

Here, we present the results of detailed CGI laboratory studies of three commercial KHIs (termed A, B & C) for a real gas-condensate (GC) production system. Products were initially investigated in detail using a generic s-II/s-I forming binary 98% CH₄ / 2% C₃H₈ natural gas analogue, before subsequently being tested with a multicomponent/multi-structure forming natural gas (NG) system at field target dosages. All experiments were undertaken with real field condensate, and in the presence (both gases) / absence (binary gas) of incumbent corrosion inhibitor (CI), to assess the effect of this on performance.

In support of hydrate structure playing a key role, a high consistency in failure subcoolings relative to s-I phase boundaries was found between the different products / gas systems, implying an ultimate inability to inhibit this structure rather than the more stable s-II. Results of detailed binary gas system studies support such a hypothesis. Here, KHI-A was found to completely inhibit s-II (CH₄-C₃H₈) growth, with failure clearly resulting from s-I hydrate formation. As a direct result of this, upon heating to generate CGI method residual hydrate fractions, PT conditions had to be kept close to the s-I boundary (as opposed to s-II), lest all hydrates / 'history' be lost, and performance on re-cooling be misleading high / poorly reproducible. In effect, KHI-A resulted in (s-II) 'hydrate history elimination', or more specifically prevented this developing, which is unusual for KHIs, and has significant implications for both field use and laboratory testing. The presence of CI appeared to stop such behaviour, seemingly by encouraging the growth of s-II hydrates and the preservation of these on heating, making residual hydrates/history retention control simpler. Consistent with a notable CI-hydrate interaction, the corrosion inhibitor had an overall positive effect on KHI-A performance.

KHIs B and C were not subject to the same 'history elimination' issue as A, while the inhibition performance of both products was likewise largely unaffected by corrosion inhibitor, suggesting a general generic KHI compatibility for this CI chemistry. With respect to hydrate structure, KHIs A & C highest performance CIR regions appeared most closely related to the primary s-I boundary for the test gas used, although this is not the case for KHI-B, which showed markedly greater efficiency in the natural gas system. For the NG case, a larger number of hydrate phases/structures may form, and it may be that KHIs A & C are more susceptible to these.

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Effect of Gas Composition on Hydrate Growth Rate and Agglomeration Tendency

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While the past decade has seen significant advances in kinetic hydrate inhibitor (KHI) evaluation, gas hydrate AA (anti-agglomeration/agglomerant) / natural transportability testing remains notably disparate by comparison, suffering from a lack of standardisation and persistent gaps in knowledge regarding the generic fundamentals of hydrate plugging. This problem is in a significant part responsible for the more limited use of AA based approaches as a hydrate mitigation strategy – be that by chemical treatment or utilising natural transportability properties – when compared to complete hydrate inhibition by KHI / THI (thermodynamic inhibitor) injection.

Historically, AA studies have primarily focused on the liquid hydrocarbon and aqueous phases, with oil composition (notably the presence of natural surfactants), water cut and salinity seen as the main controlling factors. In contrast, much less attention has been paid to the gas and hydrate phases, particularly the compositions of these.

Following delineation of the hydrate phase boundary, either by measurement or prediction, the gas is generally only considered in terms of total moles consumed for the purposes of calculating the fraction of solid hydrate formed. The hydrate phase is treated in a similar manner, being assumed as a single structure of largely fixed composition ('s-II natural gas hydrates'...'s-I methane hydrates'), with the fraction present viewed as the dominant controlling factor in plugging.

However, recent work in an ongoing industry funded JIP (joint industry project) demonstrates that both gas and hydrate composition play a major role in slurry transportability, controlling the rate of hydrate growth, plugging tendency, and LDHI performance (both AAs and KHIs).

As described in a companion article, in both single (e.g. methane) and multi-component gas systems, rather than just one hydrate phase forming, a number of hydrates of differing composition/structure nucleate and grow at variable (by up to one order of magnitude) rates as subcooling is increased, including a largely unknown low pressure s-II methane hydrate. The relatively rapid growth rates of some phases means that hydrates formed initially may not be the most thermodynamically stable, making subsequent solid-solid and/or complete dissociation-reformation transitions a common feature. Crucially, different gases show variable plugging tendencies as a function of subcooling for identical test conditions, and it is proposed that this is structural and/or structure change related, e.g. through melting/regrowth cementation mechanisms. These structure related plugging processes also give rise to novel 'un-agglomeration' behaviour, where 'plugs' disintegrate to flowing slurries at fixed PT, sometimes well inside the hydrate region, for both gas-water and gas-liquid hydrocarbon-water systems.

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Clathrate Hydrates for the Separation of CO₂ and CH₄ from Biogas: Study of Potential Kinetic Promoters

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Biogas represents a promising renewable resource that has the potential of reducing the extraction and utilization of fossil resources with the advantage of being produced in a green way [1]. Currently, most of the technologies proposed to purify the biogas to biomethane adopt systems where the environmental and human's health risks are high, e.g. use of toxic chemicals (amine scrubbing), high pressure processes (pressure swing adsorption) etc. Clathrate hydrates are water-based solids in which small guest molecules (e.g. methane, carbon dioxide), are trapped into a hydrogen bonded, crystalline structure [2]. Hydrates are mainly studied because their formation causes plugs in oil and gas pipelines, representing a major problem in the gas and oil industry [3]. At the same time, the formation conditions of temperature and/or pressure, which are relatively mild, result in a safe and easy process for gas capture/separation/purification [4]. The upgrading of model biogas mixtures by gas hydrates has recently been considered as a safe alternative to high-pressure or liquefied gas storage, and as an economic, chemical-free process for the separation of gas mixtures [5].

In this work, several factors affecting the driving force to hydrate formation are considered, such as the driving force and the presence of chemical promoters. Raman spectroscopy of the most promising surfactants was performed to characterize the formed hydrates. Separation experiments were conducted under pressures of 4 and 2.5 MPa at 274 K, under either pressure-dropping or constant pressure conditions. Results show that the separation ability of clathrate hydrates as determined by the separation factor *S* is highest when no promoters are added to the water phase; the well-known promoter sodium dodecyl sulfate (SDS) shows a value of *S* which is approximately half the value of that in pure water, while higher separations were obtained with some lignin derivatives and a non-surface-active naphthalenesulfonate derivative. We also show that the contribution of CO₂ solubility in water to *S* is important in the overall process. Finally, the separation ability of hydrates seems to be inversely proportional to the amount of gas mixture enclathrated.

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Advances in Environmental Profile for Anti-Agglomerant Low Dosage Hydrate Inhibitors (AA-LDHIs)

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AA-LDHIs have a strong track record of over a decade of use in preventing hydrate blockages in both continuous and shut-in/start-up scenarios in the offshore environment. The chief requirement for chemistry selection is usually performance of the product in the system; however, secondary properties, such as effect on corrosion, materials compatibility, compatibility with other production fluids, and water quality, are becoming increasingly more important. Additionally, for more highly regulated regions, AA-LDHIs cannot be used at all due to an unfavorable environmental profile. In these regions, producers rely on thermodynamic inhibitors (THIs) such as methanol or MEG, but, as water cut increases over the lifetime of the well, the amount of THI necessary for treatment quickly surpasses maximum pumpability limits, eventually forcing producers to shut-in these wells. An acceptable AA-LDHI would enable multiple additional years of commercial production of these systems, though there are many challenges associated with the practicality of synthesizing an industrial scale environmentally-friendly AA-LDHI. Despite these challenges, intense developmental effort into molecular design have produced a novel AA-LDHI molecule that is scale-able and has favorable environmental testing at the 2,000 L batch scale. In addition to the exceptional environmental profile, the new AA-LDHI maintains strong performance as well as favorable water quality and secondary properties.

AA-LDHIs discussed within were performance tested in hydrate rocking cells. Environmental testing was run by third party laboratories. Additional testing, including water quality testing, product formulation stability and umbilical application testing was completed in-house and utilizing standard industry techniques.

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Hydrate Management by Pore-Sealing in Oil-Continuous Systems

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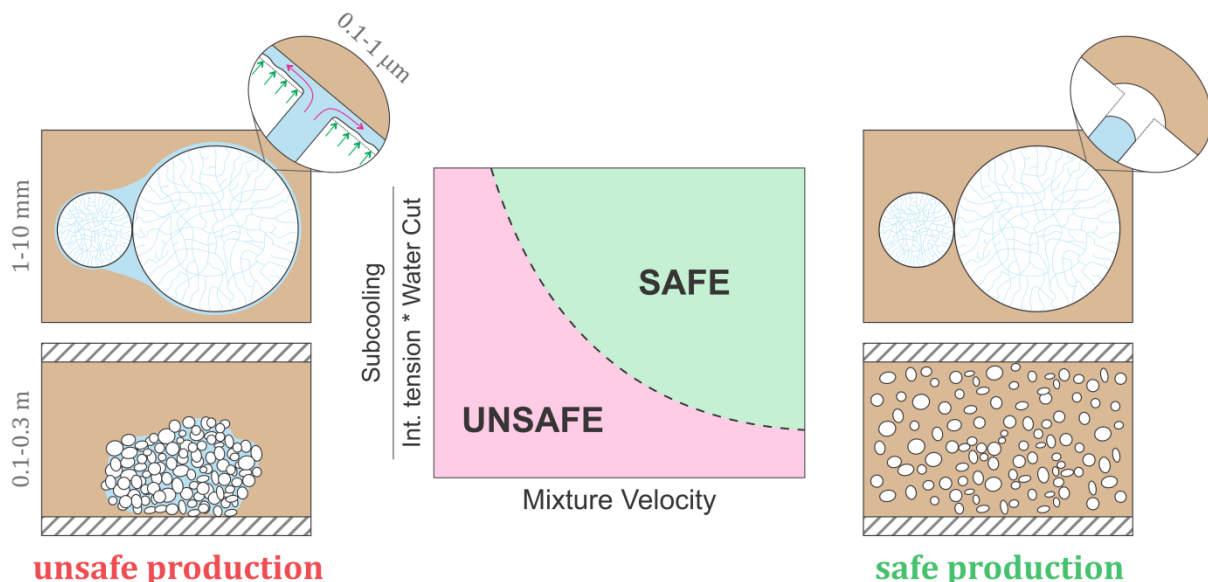
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Hydrates forming in flowing systems are very porous and, because of its hydrophilic nature, such crystals entrap a tremendous quantity of water. In oil-continuous systems, water vanishes as a free phase after the onset of hydrate formation in the time lapse of a few seconds. For agglomeration to happen, water therefore needs to permeate the porous crystals and to spread over the outer surface of the particles, forming liquid bridges (graphical abstract, left). *If one is however able to consistently seal all water content inside the particles, ceasing its availability to form the bridges, agglomeration can be prevented.* Such phenomena occur at the pore level, and key parameters are the subcooling acting on the pore sealing rate, and additives with surfactant properties acting on the water permeation rate (graphical abstract, right). By means of multiscale modelling, the pore-level comprehension was extended to estimate agglomeration at the particle-scale, and then slurry transportability at flowline-scales, with application to the oil and gas industry in the context of hydrate management. Further mathematical simplification gave rise to the *hydrate slurry phase map* (graphical abstract, center), which determines a zone for safe production, where particles do not substantially agglomerate, and the slurry remains fully suspended, thus minimizing the risk of plugging.



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Gas-hydrate reservoir characterisation through joint interpretation of geophysical data in the Danube deep-sea fan, Black Sea

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Assessing gas hydrate reservoirs requires reliable estimates of both the gas and gas hydrate concentration, which are difficult to measure directly in the subsurface. Here, we demonstrate the power of joint interpretation of various geophysical techniques and geological laboratory experiments for the Western Black Sea. 2D and 3D multichannel seismic reflection data provide detailed images of two working areas, the buried S1 channel-levee system at 1500 m water depth - well within the gas hydrate stability zone (GHSZ) - and a slope failure location, located at 665 m water depth (top limit of the hydrate formation) next to the S2 channel. Detailed compressional and shear wave (Vs) velocity-depth models were derived from four component ocean-bottom seismic data, the latter from P- to S-conversion upon reflection. Due to their steep reflection angles, shear wave events result in shorter illumination intervals of the Vs models. Nevertheless, in case of a change in elasticity of the sediment matrix due to gas hydrate cementation, shear wave events can be used as an indicator for hydrate formation throughout the GHSZ. Common reflection surface, normal-incidence-point tomography and full waveform inversion techniques were applied to enhance model resolution for the seismic data sets. 2D and 3D controlled-source electromagnetic measurements provide volume information of the resistivity-depth distribution. Electrical resistivity of the sediment formation depends on its porosity, the resistivity of the pore fluid and the saturation of the pore fluid within the pore space. Gas hydrate and free gas generally have much higher electrical resistivities than saline pore fluid, and can be assessed using empirical relationships if the porosity and pore fluid salinity are known. Calibration with logging data, laboratory experiments on hydrate- or ice-bearing sediments, and resulting velocity and resistivity values, guide the joint interpretation into more accurate saturation estimations.

The integrated interpretation of these individual data sets, their joint application, the equilibrium conditions and preservation of bottom-simulating-reflectors result in a description of the variability of the gas hydrate distribution along the Danube Fan margin. Obviously, location and depth level along the slope of the Danube Fan have distinct consequences on gas hydrate accumulation, although both areas are characterized by multiple bottom simulating reflectors. In the first working area we located two depth windows with indications for moderate 16 % to 24 % gas hydrate formation, but no vertical gas migration. In the second working area we observed fluid migration pathways and active gas seepage, limiting gas hydrate formation to less than 10 % at the BSR. Some discrepancies remain between seismic-based and electromagnetic-based models of gas and gas hydrate distribution and saturation estimates, indicating that further in-situ investigations are still required to better understand the gas hydrate systems at our study areas and to calibrate the inversion processes.

Could mixed carbon dioxide and propane hydrates form structure I?

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Could mixed carbon dioxide and propane hydrate form structure I hydrate in addition to the usual structure II? This is the question raised by some initial observations from batch reactors when dealing with mixed hydrate thermodynamics. As example, fig. (1) presents the mixed CO₂/propane hydrate composition at different temperatures and about same initial gas mixture. A significant gap in propane composition at around 4.5°C was witnessed in these experiments.

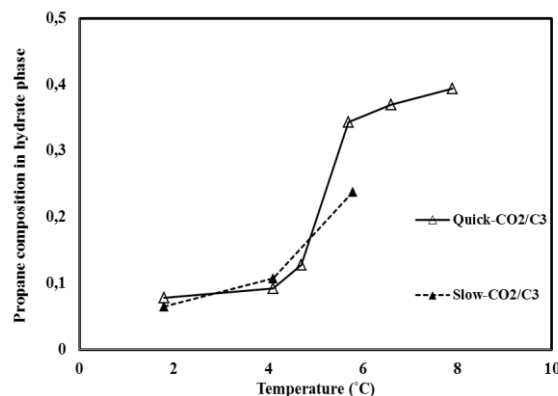


Figure 1. Propane composition in the CO₂/propane mixed hydrate phase at different temperatures for an initial gas mixture of 95.6%mol (quick crystallization process) and 93.2%mol CO₂ (slow process).

Since a structural transition could have been an explanation to this phenomenon, subsequent investigations have been carried out by means of Raman spectroscopy under isochoric and isobaric conditions, and powder neutron diffraction. Under similar conditions, Raman spectroscopy showed noticeable shifts for propane (C-C and C-H stretches). There was a prominent shift for C-C band of propane at 876cm⁻¹ (instead of 869.6cm⁻¹). In addition, two peaks for C-H bond instead of a single peak was observed for pure propane hydrates (at 2881.5 and 2886.7cm⁻¹). Powder neutron diffraction analysis revealed that the mixed CO₂ - C₃D₈ hydrates exhibited characteristic Bragg peaks of coexisting SI and SII clathrate structure.

All these observations have led to a very likely conclusion. Propane and carbon dioxide hydrate could form structure I hydrates instead of structure II for high CO₂ concentrations at appropriated temperature range.

Since propane is an interesting potential promoter for hydrate-based technologies, such results need to be taken seriously into consideration when designing an industrial process.

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Equilibrium properties and phase behaviour of carbon dioxide hydrate from Monte Carlo simulations in the Gibbs ensemble with machine learning assisted analysis

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Abstract

In this work, we examine gas hydrates of carbon dioxide via Monte Carlo simulations. Taking advantage of the latest breakthroughs in phase behaviour analysis techniques and machine learning methods we take a detailed view of the properties and characteristics of the hydrates of carbon dioxide at the molecular scale. Simulating these systems in the isothermal-isobaric Gibbs ensemble we can separate the gaseous carbon dioxide phase from the water-rich phases of structure I and II hydrates of carbon dioxide. By allowing the gas and hydrate phase to reach equilibrium we then obtain large and small cage occupancies and phase stability predictors. Further to this, we extend our analysis via machine learning methods to accurately predict which hydrate structure is present using only the water molecule position and orientation data.

Background and motivation

Carbon dioxide capture and sequestration is a vital component of the multifaceted approach to limit and reverse anthropogenic climate change. In this regard, the role of gas hydrates in both the capture and storage processes has great potential to meet these demands as we transition towards a carbon-neutral energy mix and meet global targets to reduce emissions in the short term. The capture of carbon dioxide from fossil fuel combustion or via direct air capture processes is one half of the solution. This goes hand in hand with technologies for long term geological storage. The motivation of this work is therefore to analyse the suitability of carbon dioxide hydrate as a medium for carbon capture and long-term storage. To this end, our work aims to examine the phase stability and equilibrium properties of carbon dioxide hydrates.

Research presented

This presentation will cover our studies of carbon dioxide hydrate. We employed Monte Carlo numerical simulations in the Gibbs ensemble to model the two-phase equilibrium between carbon dioxide and hydrate phases. Equilibrium properties were measured, and a direct comparison was made between the stability of the different hydrate structures. In addition, we applied machine learning methods to correctly identify which type of hydrate is present in each simulation using data from molecule positions.

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Hydrate Formation in Aqueous Solutions Undersaturated with CO₂

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CO₂ injection in geological formations is a key aspect of the CCS strategy. The injection and the potential CO₂ expansion can be associated with a large Joule-Thomson effect and may in turn pose a risk of hydrate or ice formation in the formation due to the cooling effect. Beside, CO₂ can be injected/stored through the Carbonated Water Injection technology, where CO₂ from offshore power production is captured from the flue gas and compressed/injected into the geological formation as dissolved gas in the injection water. Hydrate could be formed in the injection water with dissolved CO₂.

The objective of the work was to obtain experimental data on the hydrate equilibrium (melting) temperature (HET) of aqueous phases undersaturated with CO₂, at different CO₂ saturation levels and with different aqueous phase compositions (sodium chloride and sodium chloride/calcium chloride). In the case of HET there is currently no data published in open literature yet. This paper details the experimental equipment, methods, test fluids and results. To study the phase equilibria of CO₂-brine systems and further validate the results, solubilities of CO₂ in different concentrations of NaCl aqueous solutions were measured in the low temperature region and over a wide range of pressure. Experimental results were compared against predictions of the simplified cubic plus association equation of state (sCPA-EoS) coupled with the van der Waals and Platteeuw solid solution theory.

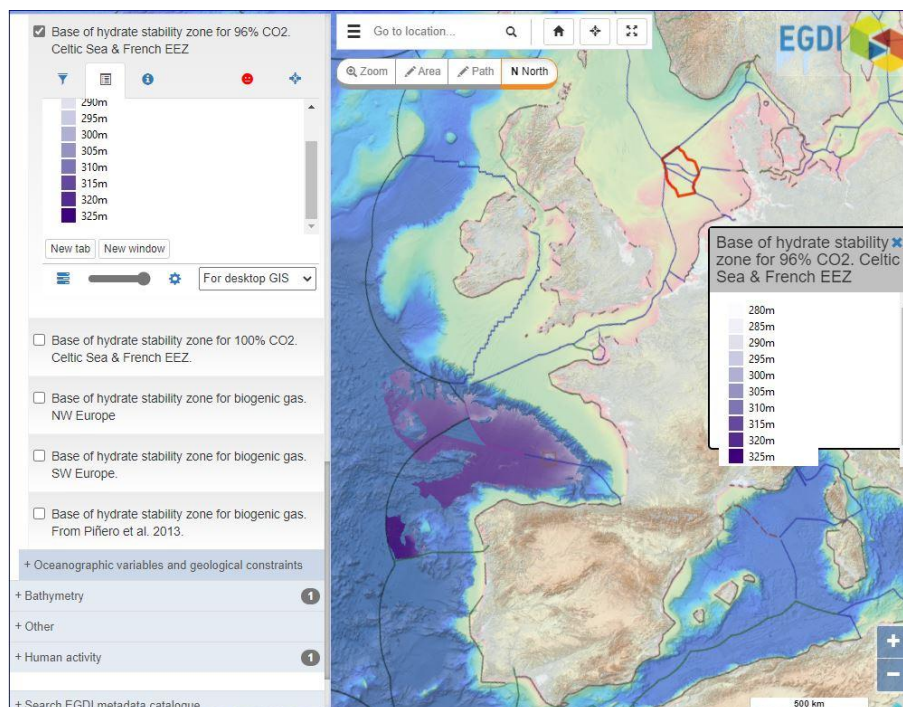
Key words: Carbon dioxide; solubility; hydrates

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Potential safe geological storage of CO₂ as mixed gas hydrates along the European continental margins

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A pan-European GIS focused on gas hydrates has been developed in the GARAH project (<https://geoera.eu/projects/garah4/>) to assess for the first time the gas hydrate related risk along the European continental margins. Several factors and variables have been taken into account to assess the abundance of sediment-hosted gas hydrates and to estimate the safe storage volume of CO₂ as mixed gas hydrates in deep-sea sediments. The baseline scenario is that gas hydrate occurrence is only possible in seafloor areas where pressure (bathymetry) and seafloor temperature conditions are inside the theoretical gas hydrate stability zone (GHSZ) and that the injected CO₂(l) is expected to percolate downwards or upwards to the neutral buoyancy level (NBZ) depending on the CO₂ quality and on the seafloor depth. In the Bay of Biscay, the safe CO₂ deep offshore storage capacity is estimated in both cases (pure CO₂ or 96%ml CO₂). The French EEZ storage volume estimate of 3,422 km³ is of the same order of magnitude as the total Spanish EEZ storage volume estimate of 3,700 km³. There is, however, a big difference resulting from the seafloor depth: in the French zone, almost all the stored volume is occupied by gas hydrates, whereas in the Spanish zone, about the half (1,728 km³) is occupied by CO₂ in hydrate phase and the other half (1,972 km³) by liquid CO₂. This GIS-database has been conceived as a first step or base-line for future gas hydrate related research.



Acknowledgment GARAH project. GeoERA - GeoE.171.00

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Seafloor methane emissions in the Western Black Sea basin

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Methane gas emissions were broadly reported in the Western Black Sea sub-basin. Majority of the reported sites is dominated by methane gas originating from biogenic sources, i.e. relatively shallow in-situ organic matter degradation. However, basin-scale estimates on the amount of released methane were not yet performed. Here, we use the advantage of the 3D numerical reconstruction of the Western Black Sea basin which enables to calculate the rates and total amounts of hydrocarbon seepage at the seafloor throughout the basin history and up to a present day. The model accounts for both biogenic and thermogenic methane formation in the source rocks, gas expulsion and migration towards the upper sedimentary layers and further to the seafloor. Due to adaptable, dynamic changes in temperature and pore water pressure caused by transient environmental factors (e.g. various bottom water temperature trends, sea-level variations), the model enables the feedback from changing methane solubility conditions, or gas hydrate de-stabilization. Figure 1 presents the rates of biogenic (upper panel, violet line) and thermogenic (lower panel, blue line) methane seafloor emissions estimated from the most plausible 3D modeling scenarios. In this contribution, we discuss the magnitude and geological situation conditioning methane generation, migration, and expulsion from additional sources, e.g. previously formed gas hydrate deposits. Moreover, we are presenting the most probable basin-scale estimates of the total amounts of hydrocarbon released throughout the basin history (98Ma – present) as well as the alternative scenarios.

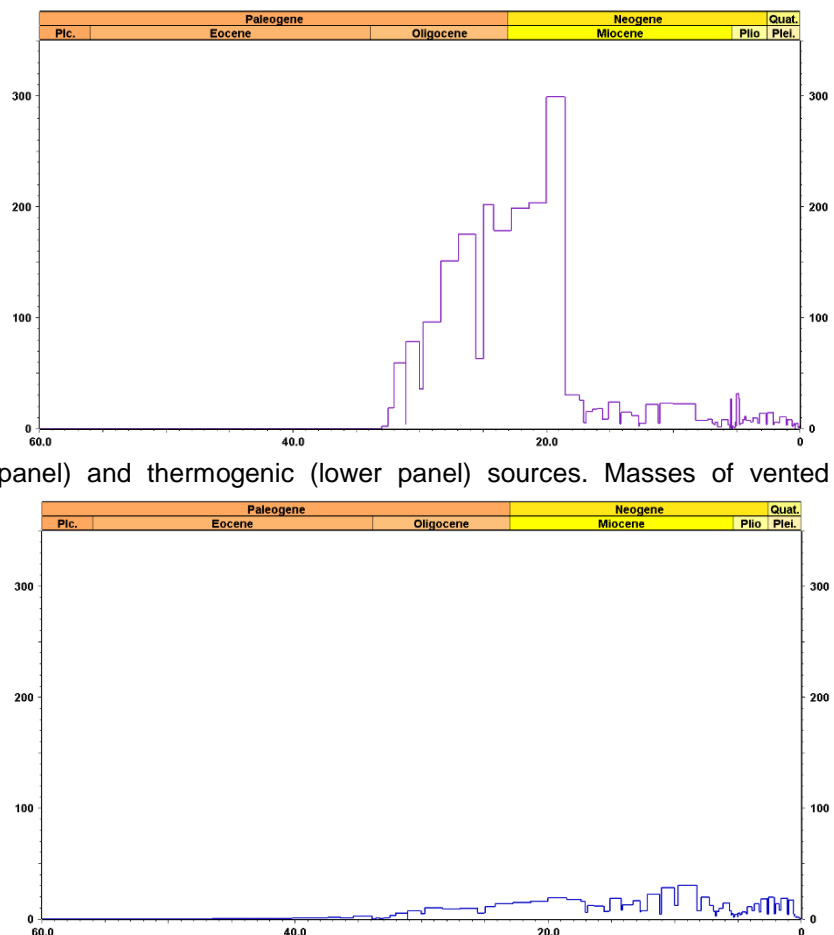


Fig. 1. Seafloor methane emissions from biogenic (upper panel) and thermogenic (lower panel) sources. Masses of vented methane are given in Gt (Y axis), whereas the time line is in Ma (X axis).

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Basin-scale gas hydrate estimates in the Black Sea derived from 3D modelling

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Complex natural gas hydrate systems of the Western Black Sea sub-basin are dominated by gas hydrate deposits located in the sandy deep-sea paleo-fans (e.g. Danube delta fan). According to the data collected in-situ during regional scientific cruises, the majority of hydrate forming methane has biogenic origin. However, several sites located more towards the open basin exhibit the ongoing seepage of higher hydrocarbon gases, mostly due to the presence of thick organic-rich Oligocene-Lower Miocene Maykopian series. Yet to this point in time, basin-scale migration pathways for both deep thermogenic as well as relatively shallow biogenic gases remain unexplored. With our 3D petroleum modeling project executed within the framework of the German SUGAR project, we designed and applied a basin-scale numerical representation of the Western Black Sea natural gas hydrate system. With the model, we are able to simulate the entire sub-basin history from 98Ma up to the present including sediment deposition, compaction and folding, deep-sea fan evolution, organic matter cracking at the great depths, in-situ biogenic methane generation at shallow depths, and multi-component multi-phase migration from the multiple source rocks towards the seafloor. Figure 1 presents the present-day estimate of gas hydrate saturation in vol. % across the western sub-basin. This gas hydrate distribution exposes different hosting conditions of gas hydrate-bearing sediments, such as moderate (~50 vol. %) concentrations in the sand-dominated deep-sea fans due to lithological contrast between the sediments, or elevated to high gas hydrate concentrations (~70-80 vol. %) in the local plateaus due to hydrate recycling and migration along the bathymetry gradients towards the shelf areas. In our presentation, we discuss various gas hydrate formation mechanisms in the Black Sea depending on the regional sub-basin geometry, availability of high-permeability migration pathways, organic matter sources, and other factors. Moreover, we present the first basin-scale estimates of gas hydrate resources in the Black Sea based on fully-resolved source rock maturation scenarios.

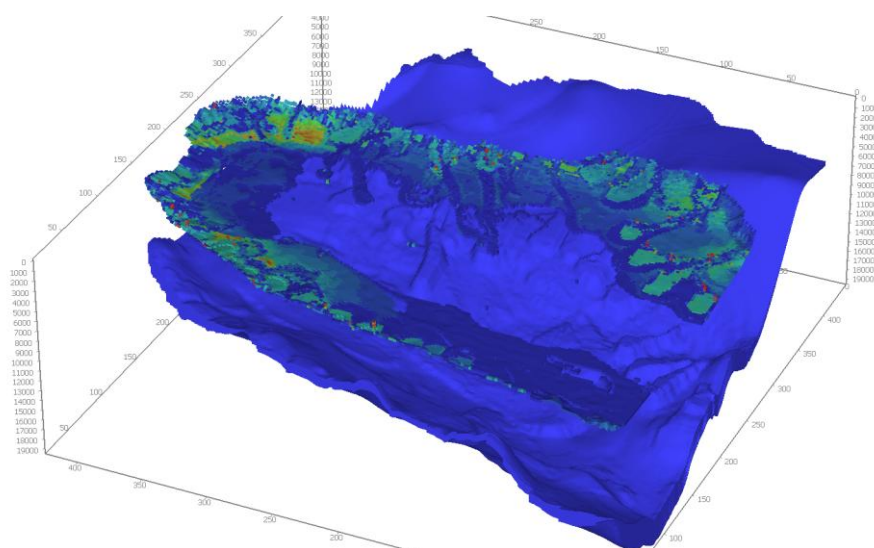
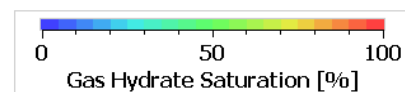


Fig. 1. Gas hydrate saturation presented in a 3D-view mode across the Western Black Sea sub-basin. The solid blue horizon projected below gas hydrate deposits presents the lowermost and the oldest Upper Cretaceous sedimentary layer included in the basin model deposited directly on the basement.



Formation of Gas Hydrates: the effect of the main natural parameters

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Because the salts inhibit the formation of natural gas hydrate and it is well known that hydrate nucleation occurs preferentially in a region with low ion concentration, the investigation about the chemical composition of seawater containing NGHs is very important to obtain useful information for the comprehension of their formation mechanisms in the natural environment.

In order to obtain this information, we studied the chemical physical characteristics of sea water present in some marine sediment samples that contained NGH collected in National Antarctic Museum in Trieste; these were analyzed and properties such as pH, conductivity, salinity, and concentration of main elements of water present in the sediments are collected. These results were successively used to determine the thermodynamic parameters and the effect on salinity of water on hydrates' formation.

Then, hydrate formation was experimentally tested using a small-scale apparatus, in the presence of two different porous media: a pure silica sand and a silica-based natural sand, coming from the Mediterranean seafloor. The experiments proved that the classical pure quartz sand, commonly used in laboratories to study gas hydrate, has a very limited impact on the process and its influence may be entirely associated with its physical properties as porous medium. Then, the analyses of the natural sand TS denoted it as both a kinetic inhibitor, because of the higher time required to carry out the process and the significant reduction of hydrate formation rate with the decrease of pressure, and a thermodynamic inhibitor, considering the higher pressure and lower temperature values required. Analyses and hydrate formation experiments described in this work confirmed and illustrated how characteristics and properties of offshore hydrate sediments are strongly affected by the water and sand respective composition. Obviously, each specific site has its own characteristics and that motivated the need for more information and scientific investigations on the effects associated with the presence of certain elements or physical properties. Till now, a very limited amount of scientific works describing both the water and sediment influence on hydrate formation have been produced; the present work aims to contribute increasing the degree of knowledge in this sense. An accurate knowledge of those parameters and their specific effect on hydrate formation might be extremely useful to define in advance the best modalities to intervene on a specific hydrate reservoir.

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Water Content of Carbon Dioxide in Equilibrium with Hydrates

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Hydrate formation constitutes a central issue in gas processing and transportation for oil and natural gas (O&G) as well as carbon capture and storage (CCS), particularly in the case of CO₂-rich streams. Many companies opt for very conservative prevention strategies, with tight drying requirements (using molecular sieves instead of absorption with glycols, for example) and continuous injection of hydrate inhibitors. The lack of reliability of the available thermodynamic models at certain T and P ranges and of the devices designed for online monitoring explains such choices, as the far-reaching consequences of an off-spec stream are potentially catastrophic, leading to hydrate blockage and all the associated risks. In the case of CO₂, there is a lack of available data at low temperature, below 273.15 K, especially in the liquid phase, and for pressures above 5 -- 10 MPa. In the present work, a new analytical methodology has been used for humidity measurements in liquid CO₂ for temperatures below 273.15K in equilibrium with hydrates. The method consists of tracking water content variations in the fluid phase resulting from frost/dew formation on a surface in direct contact with the stream. A constant-volume static cell was used to reach equilibrium conditions between CO₂ and hydrate. A schematic illustration of the set-up for water content measurements is presented in Figure 1 (a). The Soave-Redlich-Kwong Equation of state modified with the simplified cubic-plus-association (sCPA) was used to predict the experimental results. Good agreement between the model and the experimental data was obtained, as demonstrated in Figure 1 (b).

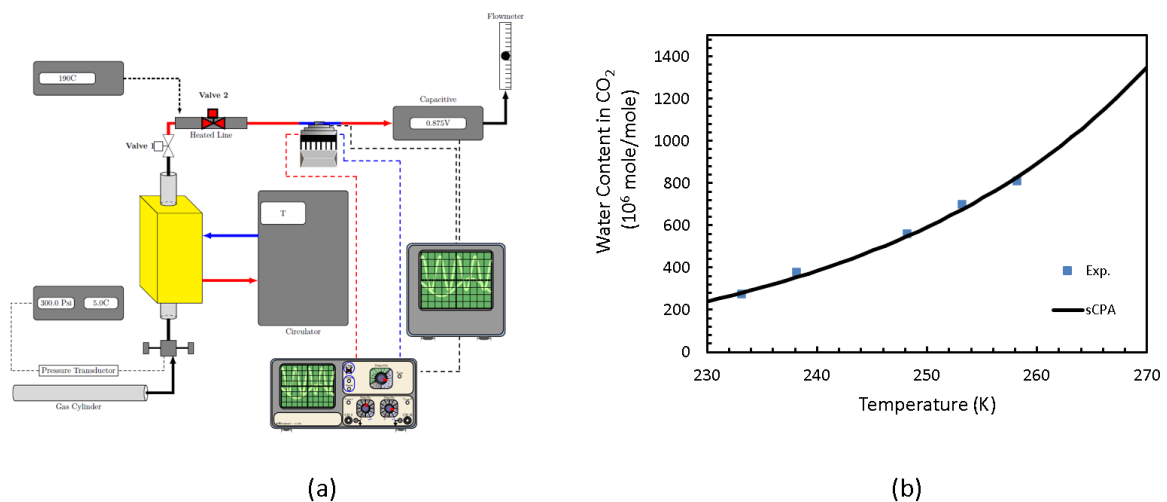


Figure 1.(a) Schematic of the set-up using a new methodology for water content measurements. The differential approach is based on recording variations of water content in the fluid phase in the vicinity of the dew/frost point; (b) Water content in pure CO₂ at 20 MPa. Predictions were made using SRK sCPA model.

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Experimental study about the Horizontal Three-Phase Solid-Liquid-Gas Slug Flow with Hydrate-Like Particles

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Oil and gas production operations often involve flows with several phases (such as natural gas, oil, water and solid particles), and these phases assume spatial configurations called flow patterns. Quite often, the operational conditions lead to slug flow as the prevailing flow pattern, which is characterized by the intermittent succession of two distinct structures: an elongated gas bubble and a liquid slug. This pattern alone can pose challenges to the equipment and connections along the production line. Another challenge is the formation of gas hydrates, whose agglomeration might block the pipeline either partially or completely, raising safety concerns and causing financial losses. The interaction between these two challenges is still unknown: how the presence of gas hydrates affects the slug flow pattern; and how the slug flow transports these solid particles. The objective of the present work is to study this interaction.

Experiments with inert polyethylene particles (with density similar to gas hydrates, 934 kg/m^3) were conducted in three different volumetric concentrations: 5%, 10% and 15%. Two different liquid phases were investigated: water and oil. Both liquid phases were tested with air as the gas phase, all under ambient conditions. To ensure the homogeneous dispersion, the particles were mixed with the liquid phase inside the liquid storage tank by means of a mixing system, consisting of a centrifugal pump and a funnel. The test section consists of a horizontal 50-mm ID, 35-m long Plexiglas pipe. Five measurement stations were assembled along the test section, composed of non-intrusive resistivity sensors in a ring-shaped configuration, to monitor the slug flow parameters throughout the experiment. High Speed Imaging was also used to analyze the flow hydrodynamics and the particle distribution. Twelve (12) combinations of liquid and gas flow rates were tested, all within the envelope of the slug flow pattern. Measurements were also performed for gas-liquid flows under the same conditions, for comparison purposes.

It can be noticed that the liquid phase superficial velocity directly influences the distribution of the particles. For high liquid superficial velocities, the distribution remains homogeneous, as presented in Figure 1 (a). At low liquid superficial velocities (Figure 1, b), the turbulent dispersion is not high enough to ensure the suspension of the particles. In addition, the particles also influence the slug flow parameters: in general, it is only a slight influence, generating small changes in the parameters, because of the liquid turbulence modulation caused by the particles. However, there are exceptional cases where this influence is greater, as the particles influence the slug flow formation.

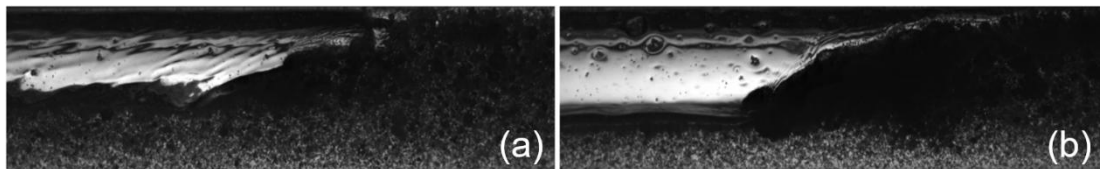


Figure 1 – Elongated bubble tails for water, 5% particle concentration, liquid and gas superficial velocities:
(a) $J_L = 1.5 \text{ m/s}$, $J_G = 0.5 \text{ m/s}$ and (b) $J_L = 0.5 \text{ m/s}$, $J_G = 0.5 \text{ m/s}$

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Rheological and thermal study of mixed CP + CO₂ hydrate slurries for refrigeration applications

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The use of gas hydrates in secondary refrigeration can reduce cooling environmental impact by greenhouse gas reduction because of their high energy density. CO₂ hydrates was selected at previous work as a candidate material for secondary refrigeration. In this study, cyclopentane, a thermodynamic promoter that has been identified for its promotive qualities to lower the formation pressure of CO₂ hydrates was used to form mixed CP + CO₂ hydrate slurries. This work deploys a temperature-controlled flowloop to characterize the rheological properties of hydrate slurries generated in situ from oil-in-water emulsions. Systems of 3 - 15wt% cyclopentane fraction to form pure CP hydrate and mixed CP + CO₂ hydrate slurries were tested. The results showed that the viscosity of CP and mixed CP + CO₂ hydrate slurries increase with the decrease of the shear rate, exhibiting a shear-thinning behavior. With a similar protocol, a rheological characterization involving a long period of hydrate slurries circulation was conducted. The results illustrated that the hydrate slurries behavior change with time. A thermal study was performed using heating tube method to determine real-time solid fractions and heat transfer coefficients for different cyclopentane concentrations.

Keywords: Gas hydrates, carbon dioxide, rheology, cyclopentane, secondary refrigeration.

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Optimization of the SCC-DFTB potential to model aqueous systems : from liquid water to gas hydrates

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Liquid water is a unique and fundamental substance with chemical and physical properties that are essential in various fields. However, despite continuous theoretical and methodological developments, its description remains challenging. In fact one has to find a compromise between accuracy and computational cost. On the one hand a large number of force fields (FF) have been developed to model liquid water, allowing large systems and long simulations but are limited as soon as explicit electronic structure is required. On the other hand, DFT has also been intensively used to model liquid water but its computational cost is hardly applicable to issues dealing with reactivity and solvation of large molecules questions. The self-consistent charge density-functional tight-binding method (SCC-DFTB) finds itself in between. The computational efficiency of this approach relies on the use of a minimal valence basis set and parametrized integrals. However, radial distribution functions (RDFs) for liquid water obtained using SCC-DFTB significantly differ from both DFT and experimental curves¹.

Cuny and co-workers demonstrated that the inclusion of Weighted Mulliken charges significantly improve the RDFs of liquid water at the SCC-DFTB level but there is still room for improvement². To do so, in combination with Weighted Mulliken charges, we implemented the iterative Boltzmann inversion (IBI) method to optimise the repulsive potential OH as described in the work of Lourenço et al³ leading to significant improvements for the O-O, O-H and H-H RDFs. The impact of these modifications of the O-H repulsive potential has been tested and validated on other liquid water properties such as self-diffusion coefficient and transfer proton energy barrier. We also implemented the IBI procedure in the framework of the Path-Integral Molecular Dynamics scheme to explicitly exclude the contribution of nuclear quantum effects to the repulsive potential. We recently applied the final $W_{\text{Mull}} + E_{\text{rep}}^{\text{opt}}$ (OH) scheme to the description of gas hydrates. I will show results on the potential energy and stability of CO₂ gas hydrates depending on the occupancy using the same method as in the work of Desmedt and co-workers⁴ with the improved SCC-DFTB potentials. We also calculated the elastic modulus and structural properties such as RDFs performing molecular dynamics simulations.

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Use of reverse micelles to enhance the formation of clathrate hydrates of hydrogen

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Hydrogen storage is a key enabling technology for the advancement of hydrogen in energetic applications, including stationary power, portable power, and transportation. To date, the main approaches for storing hydrogen are: (1) pressurization up to 70 MPa, (2) liquefaction at 20 K, (3) adsorption onto metal hydrides, and (4) complexation to other inorganic and organic compounds, which methods all have drawbacks [1]. Clathrate hydrates are ice-like inclusion compounds that form under conditions of low temperature and high pressure. In hydrates, water molecules enclose small guests such as methane, carbon dioxide, and hydrogen, among others, into a hydrogen-bonded crystal network of Eulerian polyhedra [2]. Hydrates are studied since they represent a problem in flow assurance, and their formation causes plugs in oil and gas pipelines. Besides, gas hydrates have received considerable attention as a potential means for gas mixture separation [3], and gas storage and transportation [4]. In this context, clathrate hydrates of hydrogen form at relatively low pressures (e.g., ca. 10 MPa) when a co-former compound is added and could represent a valid alternative in the field of hydrogen storage and transportation for large, stationary applications [5]. In that case, however, the gravimetric amount of stored hydrogen drops to less than 1 wt % from ca. 5.6 wt % without a co-former. Another factor restraining the entrapment of hydrogen into a clathrate matrix appears to be of a kinetic origin, in that the mass transfer of hydrogen into clathrates is limited by the macroscopic scale of the gas–water interfaces involved in their formation. Thus, the enhanced formation of binary (hydrogen + co-former) hydrates would represent a major achievement in the attempt to exploit those materials as a convenient means for storing hydrogen. We present some developments of a kinetically efficient method for preparing hydrogen hydrates, which is based on the formation of amphiphile-aided reverse micelles to reduce the size of hydrate forming gas–water interfaces down to tens of nanometers [6]. Particularly important in this approach is the chemistry of the nanoemulsion-forming amphiphiles. The reduction of particle size allowed us to decrease the kinetic hindrance to hydrate formation. The present process enhances the kinetics of the formation process and assist clathrate formation when using water-insoluble co-formers (e.g., cyclopentane, tetrahydrothiophene, tetrahydrofuran).

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Micromechanical investigations of Gas Hydrate Bearing Sediments

Eitan Cohen and Assaf Klar¹

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In view of the geotechnical problems encountered in recent field trials of gas production from hydrate reservoirs, a proper representation and understanding of the mechanical response of Methane Hydrate Bearing Sediments (MHBS) is a prerequisite for successful future gas production. Recent investigations have indicated that the increase of sediment strength, due to hydrate existence, is of frictional nature and associated with changes in the kinematic response, and not necessarily due to cementation. Following this idea, a non-cohesive micro model for methane-hydrate bearing sediments was developed, where the hydrate is represented as solid particles precisely positioned between sand particles, contributing to the skeleton response even for small strains. Analytical expressions relating between the geometry, inter-particle properties, and the mechanical response of the hydrate bearing sediment were developed. Global stress-strain response is evaluated under simulated triaxial loading, exhibiting stiffer, stronger and more dilative response compared to pure sand samples. It is shown that a trade-off exists between the particle size and the inter-particle friction, which can be unified using a participation factor related to the pore size distribution. As observed in recent experimental investigations, the suggested model results in a cohesionless response when analyzed using Rowe's stress dilatancy theory. The developed micromechanical models can be used to evaluate complex processes such as sand migration and dissociation-induced stress relaxation. The resultant (macro) response can assist in developing analytical relations for continuum-based simulations.

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Pre-screening of Protic Ionic Liquids as Hydrate Inhibitors with COSMO-RS

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Ionic Liquids (ILs) are molten salts frequently reported as hydrate inhibitors in the literature. These substances have been intensely studied in the last two decades due to their unique properties such as low vapor pressure and thermal stability, and due to their designer solvent character. Protic Ionic Liquids (PILs), despite being less costly and more easily synthesized than traditional aprotic ionic liquids, have not been deeply studied as hydrate inhibitors yet. Only a small number of PILs have been reported in the literature as thermodynamic inhibitors [1], though with efficiencies comparable to Ethylene glycol. With this in mind, the aim of this study was to pre-select PILs as possible thermodynamic hydrate inhibitors through COSMO-RS hydrogen bond energy contribution of water (H_{HB}^W) in a mixture formed by water, cation, anion and the gas, as well as the hydrogen bond energy of the PIL (E_{HB}), as suggested by Bavoh et al. (2016) and Sulaimon and Tajuddin (2017) [2,3].

The parameterization set BP_TVZP_21 was used for COSMO-RS calculations, ILs were treated as ion pairs (cation + anion). The pre-screening methodology in terms of H_{HB}^W was validated by checking for existing correlations between H_{HB}^W and average suppression temperatures (AST) of hydrate dissociation in the presence of ILs from the literature. It was noticed that the higher the modulus of the H_{HB}^W , the higher the AST, pointing to a better inhibitor. In this study, 70 PILs were evaluated as possible hydrate formation inhibitors. Besides H_{HB}^W and E_{HB} , the volumes of these PILs were taken into account in the pre-screening, since smaller cations tend to result in better inhibitors, according to the literature. Therefore, cations containing more than 4 carbons were not taken into account. The most prospective PILs selected, considering a combination of higher E_{HB} , higher H_{HB}^W , and lower volume, were $[NH_4][H_2PO_4]$, $[Pyrrolidinium][Glycolate]$, $[Ethylammonium][Glycolate]$, $[Methylammonium][Acetate]$, $[NH_4][Formate]$, which present E_{HB} higher than 100 kJ/mol and H_{HB}^W higher than 20 kJ/mol as shown in Figure 1.

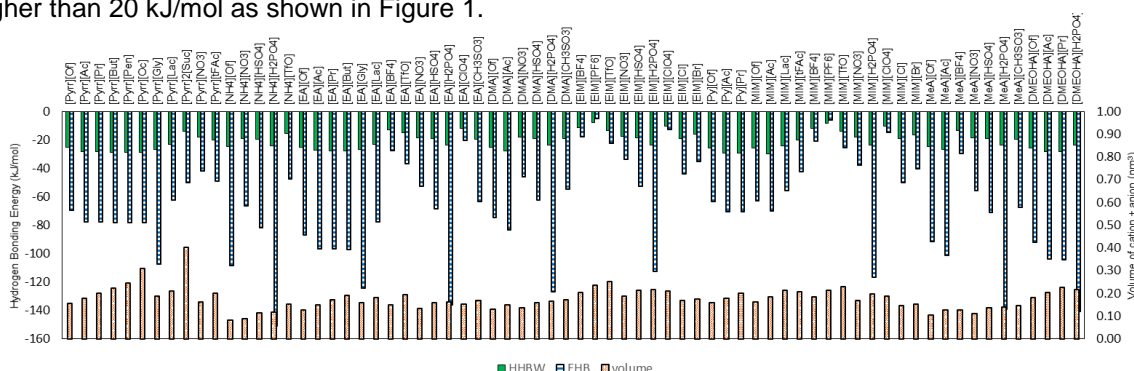


Figure 1. E_{HB} , H_{HB}^W , and volumes calculated by COSMO-RS.

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CFD-PBM simulation of hydrate growth and agglomeration in a high-pressure cell

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Abstract

The formation of gas hydrates in flowlines is undesirable in the oil and gas industry for deep-sea fields. The growth, agglomeration, and deposition of hydrates in the multiphase transportation pipeline may lead to pipeline blockage, along with production interruption and even personal safety risk. The flow assurance issue caused by hydrates has attracted considerable attention from the academic and industry community. This work employs computational fluid dynamics (CFD) and the population balance technique (PBM) to simulate the growth and aggregation of hydrate particles in natural gas and pure water systems using the simulation software Star-CCM+. A Eulerian multiphase model is adopted here to simulate velocity and physical properties of each phase at different moments, coupled with PBM model to characterize the details of hydrate particle growth and flow behavior considering the agglomeration and fragmentation of hydrate phase. The diameter distribution and aggregation degree of natural-gas hydrate particles in an agitated high-pressure cell are obtained at 100 rpm. The scheme is validated through a comparison of simulated results with experimental data in terms of hydrate volume fraction and granulometry of hydrate phase. These preliminary findings explain the evolution of hydrate particles, which can facilitate the understanding of the mechanism of hydrate blockage.

Keywords : CFD-PBM simulation, Natural gas hydrates, Agglomeration, Growth, Flow assurance

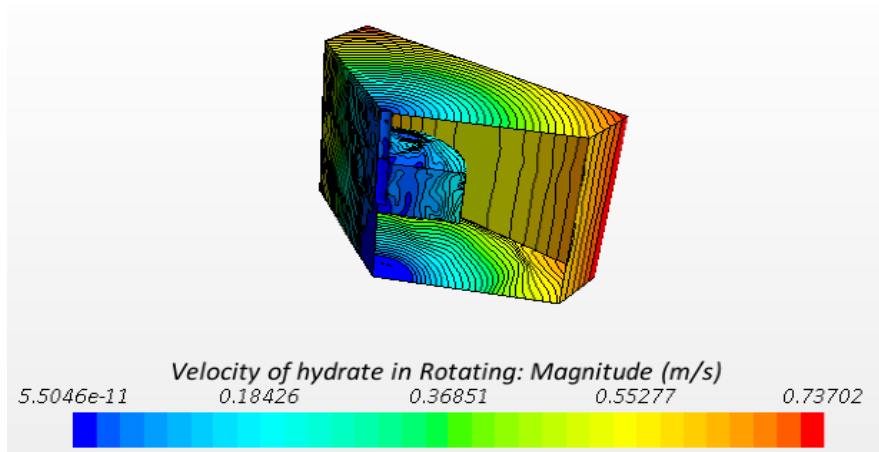


Fig.1. Contours of hydrate velocity

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A method for quantitatively evaluating hydrate blockage risk in water-in-oil emulsion flow

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Abstract

Hydrate blockage has become a vital flow assurance issue in the oil and gas industry. How to quantitatively evaluate the risk of hydrate blockage based on the specific work condition is a hot topic. In this paper, a quantitative evaluation method of hydrate blockage risk is proposed by considering the forces of hydrate particles in flowlines based on hydrate blockage mechanism analysis. Hydrate blockage experiments with different water cut, anti-agglomerants (AAs) content, and pressure conditions were carried out in a high-pressure flow loop equipped with macroscopic and microscopic measurements. Based on the mechanism of hydrate blockage, the force of promoting and inhibiting the accumulation of hydrate particles was analyzed on the premise that all the formed hydrate was deposited on the pipe wall, and the model of hydrate blockage risk was established. According to the change of flow characteristics such as flow velocity, viscosity and hydrate volume fraction, the hydrate blockage risk index (HBRI) was proposed to define the critical state of hydrate blockage, and it is found that hydrate blockage eventually occurs when HBRI exceeds 3. This method can provide reference for hydrate plugging risk assessment and optimizing hydrate risk management strategies.

Keywords : Natural gas hydrates, Blockage risk, Quantitative, Flow assurance, Force

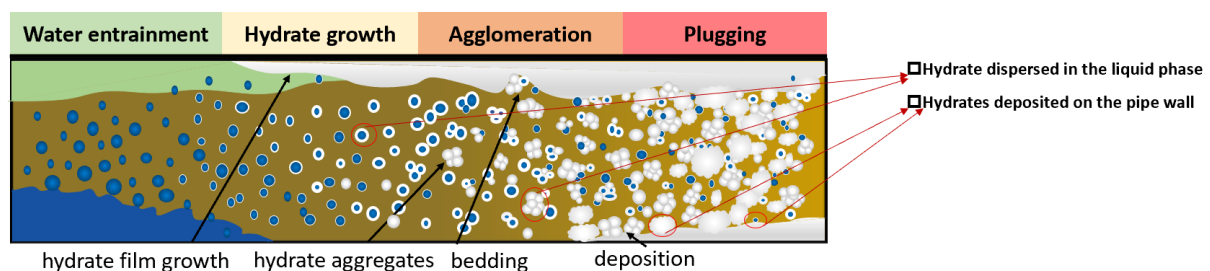


Fig.1. A Conceptual picture for hydrate formation and blockage in water-in-oil (w/o) emulsions.
Reproduced from Turner (2005).

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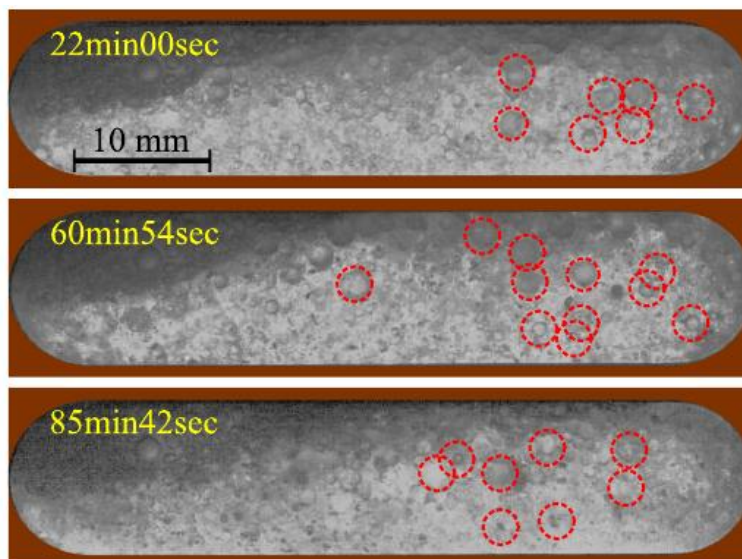
Mechanisms of hydrate blockage in oil-water dispersions based on flow loop experiments

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The formation of gas hydrates is an issue that may be hazardous for oil and gas production. In this work, new insights for the mechanisms of hydrate formation and hydrate blockage in oil-water systems are proposed, based on a series of flow loop tests at 30%, 50% and 80% water cut (volume water fraction in an oil-water system). The experiments were conducted with Kerdane oil, saline water (with 30 g/L of NaCl) and natural gas at 75 bar and 4 °C. The use of several instruments on the Archimede loop, such as acoustic emission, permittivity probe, and Coriolis, to cite a few, allowed us deducing the continuous phase, detecting the phase transporting the hydrates as well as the mechanisms of plugging as a function of the water cut (figure). At low water cut, we observe that hydrates behave as very porous structures that entrap the water phase, causing the rapid formation of large pockets flowing in the oil continuous phase and leading to plugging. At high water cut, some hydrates entrap the oil droplets and some other break apart to flow in suspension within the water continuous phase. Finally, we introduce a simplified model to estimate the local hydrate fraction, which can be used to predict plugging by monitoring its local peaks.



Experiment at 80% water-cut and 200 L/h. Images from the high speed camera at different time steps showing hydrates in red.

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A Gibbs free energy model of phase equilibrium including gas hydrates

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Gas hydrates is shorthand for clathrate hydrates of natural gas, which are solid, crystalline molecular complexes formed from mixtures of water and low molecular weight compounds.

This work presents a model of the Gibbs Free Energy of Mixing (GFEM) of hydrates, used in the framework of multiphase equilibrium calculations by means of the minimization of the GFEM. Such an approach was previously used for phase equilibrium calculations involving the three states of matter - namely, solid, liquid and vapor [1] - and has been improved in this work to also account for the hydrate phase.

The GFEM for the hydrate phase has been expressed as suggested by Englezos and Bishnoi [2], who focused on the phase behavior of the methane-water system with respect to gas hydrate formation. The GFEM for the hydrate phase combines the fugacity of the guest component and the chemical potential of water in the hydrate phase, calculated using the model first presented by van der Waals and Platteeuw [3]. In this work, the analytic fourth-order Equation of State (EoS) proposed by Yokozeki [4] has been used for the fugacity in the solid, liquid and vapor phases. This EoS offers the advantage of describing the three states of matter simultaneously with the same Equation of State, without using a different approach for the solid phase [5,6].

The proposed model, with properly regressed parameters, has been applied to the systems methane-water and hydrogen sulfide-water, which are important in industrial practice in many hydrocarbon reservoirs, especially in Alberta [7]. In order to show the reliability of the proposed approach, which can be easily extended to multicomponent systems, the results of calculations for the hydrate formation pressures are compared with both the experimental data available in the literature and the results obtained using commercially available hydrate prediction programs that make use of different approaches.

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Modeling the time-dependent dissolution of Gas Hydrates in the South Shetland Islands, Antarctica

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The numerical models can be efficiently used to simulate the behavior and stability of the gas hydrates and hydrate related free gas (methane) over time. In this study, we constructed a marine subsurface model by using two multichannel seismic reflection profiles in order to simulate the heat and fluid flow dynamics in gas hydrate bearing sediments of Offshore Antarctic Peninsula, South Shetland Islands. The finite volume method was used for multiphase numerical simulations by implementing a commercial finite volume code, ANSYS-Fluent. Sediment thicknesses, location of in-situ faults/fractures and water column thickness were directly obtained from seismic sections to build the subsurface model and to set the initial conditions. In the system, the thermal and physical rock properties such as permeability, porosity, heat capacity and thermal conductivity are assumed to be constant within each rock unit. Temperatures of rock matrix and the relevant pores are taken to be the same due to thermal equilibrium. In the construction of mesh, triangular discretization in different lengths is employed in order to create mesh structure of the referenced 2D seismic lines. The very irregular non-uniform nature of the marine sedimentation layers of our present model can be efficiently modeled and meshed by using triangular elements with different sizes wherever necessary. Several time-dependent (transient) fluid flow models are created in order to explore and evaluate the behavior and dissemination of different gas hydrates concentrations. With these models, the mass ratios of dissolved CH₄ (methane) to CO₂ (carbon-dioxide) and H₂ (hydrogen) gases produced in time are determined which is a result of the chemical interaction of hydrate-bound free gas (methane) with groundwater. Prominent effects of geological structures such as presence of in-situ faults/fractures and the thickness of sediments are revealed in the numerical models. Numerical simulations demonstrate that the dominant effects of in-situ faults in which the reactant of CH₄ is drained off very quickly while the products of CO₂ and H₂ are emitted directly through the faults. It is found that depending on the gas hydrate concentration within the sediments, dissolution time varies from hours to days. Finally, it is also observed that the dissolved methane gas is accumulated as clusters within the sediments.

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Dielectric properties of CO₂ clathrate for the Jovian system exploration

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Clathrate hydrates could be components of the crust in different icy moons. Their presence in Jupiter's satellites was proposed after the analysis of the information provided by the NASA Galileo mission. Data from this mission revealed that the Jovian moons have both, the compounds and physical conditions required for clathrate formation from the subsurface to deeper layers (Prieto-Ballesteros *et al.* 2005, Hand *et al.* 2006, Izquierdo-Ruiz *et al.* 2020). In particular, CO₂ clathrates are one of the candidates to be formed there.

At the beginning of the next decade, two space missions will be arriving to the Jupiter system to study their moons with a variety of experimental techniques on board, including radar measurements. Both missions, Europa Clipper (NASA) and JUICE (ESA), include in their payload antennas with frequencies of 60 and 9 MHz (Clipper) and 9 MHz (JUICE) with the capacity to penetrate under the surface down to 30 km in the case of the American mission and to 9 km in the European mission. Europa will be explored by both missions, although JUICE will also study Ganymede and Callisto. In order to interpret the results of the measurements is necessary to know the dielectric properties response of several materials that could be part of the crust of these bodies.

In the laboratory, we have recreated the conditions of formation of CO₂ clathrates and measured its dielectric properties. We have used a high-pressure chamber capable of controlling and recording the temperature and pressure of the sample. Inside the chamber, we have introduced a Teflon cell with two electrodes connected to a LCR-meter to measure the conductance (G) and the parallel capacitance (Cp) of the sample upon different temperature and pressure conditions. The chamber includes a sapphire window which allows us to carry out *in situ* Raman spectroscopy measurements in order to determine the formation of the clathrates.

The results allowed us to differentiate the CO₂ clathrate respect to other phases that could also be formed during the experiments. The CO₂ clathrate measured samples have a real permittivity (ϵ') of around 2.6 and a conductivity (σ) of $1.5 \cdot 10^{-4}$ S/m, both at 255 K and high frequencies. These values are similar to the defined by Stern *et al.* (2021). The attenuation of the signal, calculated at 10 kHz and using the equation $\alpha \cong \sigma / (2c\epsilon_0 \sqrt{\epsilon'})$, shows clear differences between the samples of CO₂ clathrate, water with dissolved CO₂, and water itself, with values of 10.99, 1.35 and 0.34 dB/Km at 265 K respectively.

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How ionic defects play a role on the super-protonic conductivity of strong acid hydrates.

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Designing new devices dedicated to energy storage and production is at the center of nowadays concerns. In this area, the development of new electrolyte is of prime importance. Clathrate hydrates systems represent an opportunity as a new electrolyte for fuel cells [1], for which fundamental questions are opened. Clathrate hydrates [2] possess interesting properties depending on the nature of the invited molecules, due to their nanostructuration and to their specific physical-chemistry properties [3]. In the case of gas hydrates, the guest molecules are gaseous species (CO₂, CH₄, H₂ etc) and offers new opportunities in the broad area of energy [4]. When acidic species are encapsulated, clathrate hydrates are classified as super-protonic conductor, due to the encapsulation of anionic species generating delocalized protons into the cationic cage network [5,6,7]. To better understand the conductivity mechanism, experimental and theoretical approach are combined in the cases of HClO₄ and HPF₆ hydrates – both systems being among the best conductors [8,9].

Two issues are addressed: the role played by the ionic defects in terms of concentration and of localization in the clathrate structure. It is possible to prepare mixed hydrates (i.e. encapsulating two guest species) by co-including HClO₄ acid and tetrahydrofuran (THF) molecules. By varying the ratio of THF to HClO₄, such mixed hydrates offer the opportunity to control the concentration of the acidic defects in the clathrate structure [10]. By means of impedance measurements on the mixed hydrate (1- α) THF - α HClO₄ -17 H₂O with various α concentration, it is shown that the protonic conductivity is controlled not only by the ionic defect concentration, but also by the formed clathrate structure as revealed by X-ray diffraction analysis. Regarding the ionic localization, HPF₆ hydrates exhibit molecular defects, due to the existence of impurities (e.g. H₃PO₄) associated with the high reactivity of the hexafluorophosphoric anions [8]. Locating these defects at a molecular scale and understanding their effect on the hydrate properties is a fundamental question of prime importance for improving the electrolytic properties of the strong acid hydrates. Quantum mechanics calculations have been employed for investigating such properties in the Density Functional Theory (DFT) approximation. The comparison of these theoretical results with Raman scattering and conductivity measurements [9] allows to reveal the role played by original microstructuration observed in this hydrate and the ionic defects onto the proton mobility [10].

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Clathrate hydrates FTIR spectroscopy to understand cometary ices

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Comet nuclei, when stored in the transneptunian region, are subject to heating at temperatures from 30 to 50 K over the age of the solar system. The timescale for sublimated volatiles to escape the objects at these temperatures is long though [1], so that a gas phase remains in contact to an icy matrix on such long timescales. Once these nuclei enter the inner solar system and become active, subsurface sublimation puts once again a gas phase in contact of the porous and tortuous ice structure of cometary material. In this context, the formation of clathrate hydrates may be considered as a plausible trapping mechanism of these gases, occurring in subsurface layers, and allowing some of the most volatile species to subsequently survive in cometary material at temperatures higher than the sublimation temperature of the corresponding pure solid [2].

Gas hydrates only form and remain stable in specific temperature and pressure regimes that depend on the nature of the guest molecules [3]. Theoretical phase diagram of clathrate hydrates show that it would be possible to form clathrates at very low pressure (10^{-10} bar) and temperature (< 80 K), but there is a critical lack of experimental data using these preparation methods [4]. Could clathrate hydrates be formed under conditions relevant to the interior of comet nuclei? The formation and characterisation of these ice-like structures under such conditions could provide valuable experimental evidence for understanding the preservation of some volatile species during the thermally-induced evolution of comets.

In an effort to assess whether hydrates may play a role in maintaining volatile species in cometary material, FTIR spectroscopic identification of several species have been performed. We present results related to carbon dioxide and methane hydrates, in conditions relevant to cometary nuclei, i.e. at low temperature (10 K) and pressure (base pressure 10^{-7} mbar) regimes. 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, as well as the influence of the gas mixture and the deposition method, will be presented.

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Slope instabilities and gas hydrate dissociation in the western Black Sea since the last glacial maximum

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Marine landslides, which are observed worldwide along continental slopes, constitute the most important processes reworking sedimentary deposits and a major geohazard for marine and coastal domains. They can generate potentially the destruction of marine infrastructures through the formation of turbidity currents and/or hazardous tsunamis. In the Romanian sector of the Black Sea, high amounts of methane are detected in the sediments and at the seafloor through the identification of gas seeps in the water column. They occur on the upper slope, mostly outside the large gas hydrates system occurring in the sediment below -660 m water depth, where methane is trapped in ice cages that act as a buffer zone hampering methane to reach the water column. New geophysical and geotechnical dataset acquired along the Romanian margin reveals that the active seepage zone is associated with numerous slope failures, which incised the continental upper slope. Is there a possible relationship between gas hydrate system and recent slope instabilities? Could intense free gas emissions and/or gas hydrates dissociation have triggered such geohazards? To answer these questions, we present (1) an high resolution mapping and dating of landslides since the last glacial maximum (-35 ka), (2) results of numerical modelling showing the evolution of gas hydrates stability zone inside the sediments since the last 35 ka taking into account the environmental variations that occurred during this time lapse (geothermic gradient, temperature, salinity and sea level).

The models highlight the major effect of environmental changes and particularly the glacial/interglacial cycles and salinity variations on the extent of the gas hydrates. The confrontation of those models with slide extensions, depths and ages allows to better discuss the respective influences of gas hydrates dissociation, stratigraphic overpressure and seepage on slope instability since the last glacial maximum.

Key words: gas hydrate, free gas, landslide, BSR, overpressure, detachment surface, geohazard, Western Black Sea, modelling.



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Gas selectivity of the thermogenic-like gas hydrates: experimental and modelling

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Natural emissions of hydrocarbons play a fundamental role in the dynamics of cold seeps on continental margins. They can come from hydrocarbon reservoirs located at deep depths (thermogenic origin) or generated from the degradation of organic matter in the upper sediment (microbial origin). Thermogenic gases usually contain significant amount of none-methane hydrocarbons, as for instance, ethane, propane, butanes and condensate C5+ hydrocarbons. Thus, at favorable (T,p) conditions in the sedimentary column, they form complex multicomponent hydrates. Such a crystallization process occurs on the Western High in the Sea of Marmara where thermogenic hydrates have been retrieved at a gas emission site. Previous studies have shown that these hydrates contain more than 30% none-methane hydrocarbons, with the highest propane content even encountered in natural deposits. Such a large amount of C2+ illustrates the fractionation process that occurs during the hydrates formation, and make the Marmara hydrates a natural laboratory to study the formation mechanisms of such complex hydrates (Bourry et al., 2009; Ruffine et al., 2012). Nevertheless, to get more insights into the formation mechanisms of the Marmara thermogenic hydrates, laboratory experiments are needed.

This work is focused on the investigation of the mechanisms which govern the processes of thermogenic hydrate formation. A synthetic multicomponent gas mixture with a composition similar to the gas sample collected in the Sea of Marmara is used. The coupling of a gas chromatography analysis and high-resolution Raman spectroscopy allows the monitoring of the gas selectivity during the hydrate formation. Moreover, the molecular vibrations disclose information about the type of hydrate structure, composition and occupancy rate. This vital information is modeled using the thermodynamic Van-der-Waals-Platteeuw model.

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A new high pressure method for successive accumulation of hydrate active components

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An experimental method to accumulate hydrate-active components by successive extraction and spiking was developed. The method is demonstrated by accumulating hydrate active components from several crude oils, but could be expanded to study the activity of synthetic hydrate active components. The method developed forms hydrates in a high pressure autoclave set up at SINTEF Multiphase Flow Laboratory at Tiller. Gas hydrates in the current tests were formed utilizing crude oils with a synthetic hydrocarbon gas phase consisting of methane, ethane and propane and a 3.5 wt% NaCl brine phase. The hydrate active components were accumulated through a successive extraction of the oil and water in the hydrate phase which were then mixed with fresh oil (called spiking here) before a new hydrate formation was performed. For each successive step, samples of each phase from the oil and water associated to hydrate and the bulk oil and water not associated to the hydrate phase were collected for later analysis. The spiking procedure was repeated 4-5 times for the systems studied in this work. The presentation will describe the instrumentation and the accumulation procedure in detail. Furthermore, experimental results indicated the accumulation by showing that the spiked system increased the wetting index of the oil system. Further indications of the effect of the accumulation were obtained by performing multivariate analysis on ESI positive FT-ICR MS spectra taken of the samples.

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Yield characteristics of hydrate-sand slurry

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Keywords: Hydrate slurry, Micron sand, Yield characteristics

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Characterization of free and sediment-trapped CO₂ and CH₄ gas hydrates by Raman and SEM measurements

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Keywords: CO₂, CH₄ exchange, natural sediments, Raman analysis, morphological analysis

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Utilization of machine learning on FT-ICR MS spectra for improved understanding and prediction of the properties of hydrate-active components

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Gas hydrates consist of gas molecules trapped in cages formed by water molecules at low temperatures and elevated pressures. They are known to deposit on the wall of experimental or production equipment or self-aggregate into large lumps, where both often lead to plugging of the equipment used. If gas hydrate formation cannot be avoided, or is deemed as beneficial, the aim is to make sure that the hydrates do not deposit or self-aggregate but rather form slurries. To form stable slurries, components called anti-agglomerants (AAs) can be used to prevent gas hydrate particles from growing or depositing on other surfaces. Synthetic AAs are commonly used in the oil industry, but it has also been shown that some crude oils form hydrates that do not agglomerate or deposit but remain as transportable particles in a slurry. This self-inhibiting property is accepted to be due to naturally occurring hydrate inhibitors rendering the surface of the hydrates to be hydrophobic. Despite decades of research their structures are not yet determined. The high mass accuracy of FT-ICR MS (Fourier Transform Ion Cyclotron Resonance Mass Spectroscopy) allows for more detailed analysis of crude oil composition. Using advanced multivariate data analysis and machine learning to analyse the FT-ICR MS spectra, it may now be possible to identify these naturally occurring anti-agglomerants. Machine learning models can identify trends in data and could provide more knowledge on how and when gas hydrates are formed. Identifying properties of gas hydrates are crucial to achieve better understanding of the hydrate phenomena. A better understanding of the chemical structure of naturally occurring gas hydrates components can be used not only to help the oil industry towards less chemicals consumption, but also contribute to develop new hydrate inhibitors that can be used in emerging gas hydrate technologies in sustainable industries for refrigeration, gas separation, water treatment etc.

In this study, multivariate analysis, and machine learning methods such as Principal Component Analysis (PCA), Partial Least Squares Regression (PLSR) and Hierarchical Cluster-based PLSR (HC-PLSR) was used to decompose the data into lower-dimensional subspaces spanned by latent variables. This was done to identify components in the FT-ICR MS spectra likely related to gas hydrate formation or inhibition. Convolutional Neural Networks (CNNs), was used to extract higher level features by multiple neural layers. A combination of CNNs with latent variable-based methods (PLSR) could increase the robustness of the data analysis and increase the possibility of identifying hydrate active components.

The aim of this study was to develop machine learning methods able to correlate complex spectra from FT-ICR MS to components in the crude oil related to hydrate formation/inhibition and predict whether a new sample will form transportable hydrates or not. Developing a data science method able to predict how a hydrate system will behave holds great value for natural gas hydrates as well. Our results indicate that the models created can identify components and achieve a high prediction accuracy.

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Investigation of Dipeptides as Effective and Environment-Friendly Hydrate Inhibitors via Experimental and Computational Approaches

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The formation of gas hydrates in oil and gas stream pipelines is a great nuisance to the oil and gas industry. Low-temperature and high-pressure operating conditions in deep-sea pipelines inevitably accompany the formation of gas hydrates, which can lead to facility malfunction or fatal accidents. Consequently, various methods have been proposed to avoid or manage this phenomenon. Kinetic hydrate inhibitors (KHIs) such as polyvinylpyrrolidone (PVP) and polyvinylcaprolactam (PVCap), which retard the nucleation and growth of gas hydrates, have been used to prevent hydrate formation in pipelines. In spite of the good performance of these lactam-based polymer KHIs, they have poor biodegradability, high viscosity, and low water solubility, which can pose a threat of contaminating the ocean and be significant obstacles to wider applications. Hence, there have been extensive efforts to seek and develop nature-derived KHIs. Amino acids have been introduced as biodegradable and viable KHIs.

Dipeptides, which were composed of two amino acids with a peptide bond, have a great potential as KHIs. In this study, three dipeptides (Ala-Ala, Ala-Gly, and Gly-Gly) were presented as effective and environmentally benign KHIs for CH₄ hydrate, and their inhibition performance was evaluated using experimental and computational methods. The kinetic inhibition performance of the three dipeptides was initially assessed using a stirred high-pressure autoclave and a non-stirred high-pressure micro-differential scanning calorimeter (HP μ -DSC) by measuring the onset temperatures of CH₄ hydrate in the presence of the dipeptides. The experimental results showed that the three dipeptides (Ala-Ala, Ala-Gly, and Gly-Gly) functioned well as CH₄ hydrate inhibitors since the onset temperatures of dipeptide-containing systems were lower than that of the pure water system. In particular, Ala-Gly dipeptide was the most effective, and its performance was comparable to that of PVCap. Furthermore, the nucleation and growth of CH₄ hydrate in the presence of the dipeptides were simulated and visualized through molecular dynamics (MD) simulations. Several MD analyses including order parameters (F_3 and F_4), hydrate counts, mean square displacement, and radial distribution functions were carefully conducted to reveal the inhibition mechanism of dipeptides. The MD simulations demonstrated that the N-termini of the dipeptides were the key constituents for inhibiting the CH₄ hydrate, and the Ala-Gly-containing system had the strongest interaction between dipeptide molecules and CH₄ hydrate.

The combined experimental and computational results obtained in this study would be of great help in searching for nature-derived, environment-friendly hydrate inhibitors and provide insights into the molecular inhibition mechanisms of various hydrate inhibitors.

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Microscale investigation on methane hydrate formation kinetics: influence of sedimentary environment and NaCl.

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Gas hydrates are crystalline structures consisting of cages resulting from the hydrogen bonding of water molecules (host) enclosing relatively small gas molecules (guest), such as hydrogen, methane and other small hydrocarbons [1]. Gas hydrates occur naturally on continental margins and in the permafrost region where the pressure and temperature conditions are favorable for hydrate formation and stability [2,3]. Methane hydrates represent the largest natural reservoir of methane on Earth (with estimates ranging between 600-10000 GT). However, large uncertainties remain about the amount of methane trapped and the mechanisms governing methane fate, limiting conclusions about climate implications [4,5]. The Romanian sector of Black Sea is known to host a large amount of hydrates, and samples have been collected at around 700m water depth (70bars), where the seafloor temperature is close to 282K. Furthermore, the scientific cruises Ghass (2015) and Ghass2 (2021) conducted by Ifremer, revealed that the hydrates are formed in a clay-rich sediment. In the context of the study of the Black Sea hydrate deposit, the influence of the complex clay/sand matrix on the methane hydrate formation is studied using neutron diffraction. Methane hydrate structural properties and formation kinetics are investigated in presence of both natural and synthetic sedimentary environment and NaCl. These physical-chemistry results provide new insights on the formation mechanism, including original findings on the impact of clay chemistry on hydrate kinetics with investigations ranging from minutes to several months.

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Simulating multiple BSRs in the dynamic gas hydrate stability zone of the Danube paleo-delta, Black Sea

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The gas hydrate stability zone (GHSZ) refers to the depth interval in which the pressure-temperature-salinity (pTS) conditions allow the formation of gas hydrates (GH). Usually it is defined by the water depth at the upper boundary and by the geothermal gradient at the lower boundary. In seismic analysis, this lower boundary can be identified by the bottom simulating reflector (BSR), a characteristic seismic reflection signal running parallel to the seafloor, at the transition of solid GH to free gas. The GHSZ is dynamic and sensitive to local and regional pTS state, and can, therefore, shift in response to sedimentation processes and/or changes in environmental conditions such as bottom water temperatures, hydrostatic pressure, and porewater salinity.

In most locations worldwide, the time scales of sediment accumulation and burial suggest that the GHSZ is likely continuously reshaping under near-equilibrium conditions, leading to smoothly shifting **single BSR**. However, two or more **vertically stacked BSRs** have been reported from multiple sites around the world, often in environments with dynamic and irregular sediment deposition histories (Popescu et al., 2006; Zander et al., 2017; Ker et al., 2019). These multiple BSRs represent former positions of the GHSZ, and imply that free gas or even GH must be preserved at these paleo-BSRs below the modern GHSZ.

A prominent example is a stack of 4 well-defined BSRs in the levee deposits of a buried channel-levee system in the Danube delta. The paleo-BSR positions have been shown to correspond to former locations of the seafloor. Shifts in temperature profiles after rapid sediment deposition appear to dominate the pT conditions leading to these multiple BSRs, rather than bottom-water temperature change or sea level variations related to the isolation of the Black Sea from the Mediterranean during glacial sea level low-stands (Zander et al., 2017). While there is a consensus about the links between the multiple BSRs and sediment deposition histories, the actual multiphysics processes that could lead to the persistence of residual free gas pockets and/or gas hydrates at the paleo-BSRs over geological time scales are not yet fully understood.

In this talk, we will present results from a numerical study, performed using our newly developed high fidelity multiphysics model, that simulates the sedimentation driven recycling of gas hydrates in the Danube deep-sea fan. In particular, we demonstrate that in this dynamic sediment deposition regime sufficient amounts of residual gas can remain trapped in the former GHSZ, and discuss the state and parameter constraints under which paleo-BSRs can persist over geological time scales.

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On the existence of bifurcation manifolds in dynamical models of burial-driven gas hydrate recycling

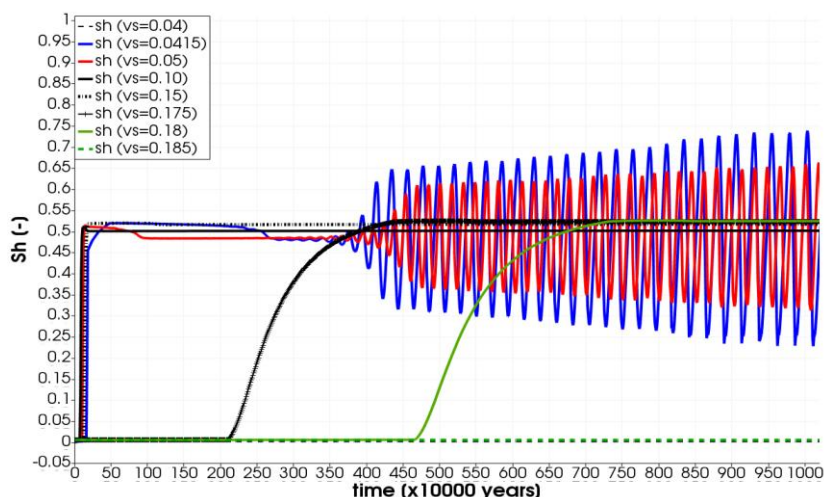
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Burial driven recycling of natural gas hydrates is characterized by complex multi-physics interactions, where the formation of distinct gas hydrate layers in the gas hydrate stability zone (GHSZ) is controlled by a complex interplay between organic matter degradation, methanogenesis, and continuous burial of phases, gas migration dynamics, and gas hydrate phase change kinetics. Conventional understanding, cultivated through simplified mathematical models, dictates that over geological time scales these processes converge to a steady state, and the corresponding hydrate distribution is widely used as a basis for constructing global hydrate inventories. However, our high fidelity model strongly suggests that the long term stability of the gas hydrate dynamical system is not quite as straightforward. Based on preliminary numerical studies, we suspect that the model has complex bifurcation manifolds located in high-dimensional parameter spaces.

To illustrate, we show a set of time-series of gas hydrate saturations (sh) sampled over a range of burial rates (also called sedimentation velocities, vs) between 0.04 and 0.185 cm/yr (Fig. 1). The long-term dynamical behaviour changes from **steady state without** hydrate formation (at $vs \leq 0.04$) to **periodic or cyclic steady states with** hydrate formation (for $0.04 \leq vs < 0.10$), to **steady state with** hydrate formation (for $0.10 \leq vs < 0.185$), and finally, back to a **steady state without** hydrate formation (for $vs \geq 0.185$). We expect similar shifts in stability for other control parameters as well, like sediment permeability, in-situ methane availability, and possibly many more.



This apparent existence of bifurcation manifolds and in particular, the periodic states, has profound implications as it sets hard limits on the predictability of present-day gas hydrates through steady-state analysis. This means that if parameters for a particular geological scenario lead to a cyclic (or periodic) steady state, we cannot say with confidence which part of the cycle we are on at the present moment. However, what we can predict is the maximum and minimum amounts of gas hydrate (e.g. 70 vol. % vs. 20 vol. %; see Fig. 1) that can occur for the given set of parameters, suggesting that there is an inherent source of uncertainty embedded in these models. Fascinatingly, the formation of hydrate within GHSZ also appears to be bounded along certain parameter axes, like burial rates as shown above, where hydrates **only** form when for $0.04 \leq vs < 0.18$. The overarching implication of these observations is that, using classical models and methods, we may be grossly overestimating the amounts of gas hydrates present globally. The existence of cyclic states also makes it difficult to predict pressure state and free gas saturation with certainty, which bears direct consequences for slope stability and other geomechanical hazards mapping.

In this talk, we exhibit and explain these dynamical properties and their implications, with a special focus on the periodic states, through a series of numerical studies covering a wide range of geological settings.

Surface Induced CO₂ Hydrate Nucleation and Growth

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Gas hydrates (GHs) are crystalline solids where the appropriate size of guest (gas) molecules entrapped within the polyhedral cavities formed by the hydrogen bonded structure of water (host) [1]. Owing to the ability of GHs to store large volume of gas, they are becoming a popular alternative for carbon capture and sequestration technology (CCS). Hydrate formation is like crystallization process and associated with stochasticity due to varied time scales of nucleation and growth. Accelerating the rate of nucleation and growth is possible by adding an appropriate chemical (surfactants) or a surface that may provide nucleation sites to trigger energetically favoured heterogeneous nucleation, which may make hydrate-based CCS technology energy efficient and economically viable [2].

In this work, we have used a rocking cell apparatus and placed 17 mm balls of materials with varying wettability namely, borosilicate glass (BG), stainless steel (SS), teflon (TF), silica nitride (SN), polyoxymethylene (POM), soda lime (SL) and polyurethane (PU) for mixing the vapour/liquid phase within the cells and measured the onset of nucleation temperatures and induction times using the constant cooling and isothermal-isochoric methods, respectively in absence and presence of different surfaces. Further, to ascertain the effect of surface area, balls of the same materials but of 5 mm size were also used for similar experiments. The role of the presence of surfaces with specific hydrophobicity and of the surface area in promoting the CO₂ hydrate nucleation is discussed.

Acknowledgement

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Study on tetra-n-butylammonium bromide hydrate formation kinetics for cold storage and transport

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As developing economies and the IT industry, energy demand for space cooling as well as data center cooling are increased. The high demand places a great need on improving the cooling efficiency for energy saving and carbon emission reduction. Phase change materials (PCMs) can store the thermal energy with phase change, which can improve the cooling efficiency. Tetra n-butyl ammonium bromide (TBAB) semi-clathrate hydrates can offer a large latent heat, suitable phase change temperature for cooling application and good recycling stability, which are considered as promising PCMs for the cold energy storage and transport. The mass fraction of hydrate in the TBAB semi-clathrate hydrate slurry (SHS), called hydrate fraction, is the parameter to determine the cold carrying capacity. A key requirement for adopting TBAB SHS in the cooling application is the ability to quantify the hydrate fraction in real-time. Previously the quantification of hydrate fraction has limitation to carry out under equilibrium state (i.e. at the end of formation process) lacking the capability of precise measurement during the continuous process. In this work, we developed a straightforward, accurate and real-time method based on electrical resistivity measurement of TBAB SHS to quantify the semi-clathrate hydrate fraction during the continuous process. The method was validated by highly repeatable results and good agreement with the conventional method under equilibrium state. Its capability quantitatively observed the TBAB SHS formation behavior with respect to the effect of temperature of the system from 1 °C to 5 °C, which is the driving force for the formation of TBAB hydrate. The hydrate fraction at the equilibrium and hydrate growth rate was increased as lowering the temperature. Interestingly, the hydrate formation behavior showed different depending on the temperature. A two-stage hydrate growth process was observed for TBAB hydrate formation with different structures of hydrate crystal at 1 °C and 3 °C that type A hydrates were preferentially formed followed by a phase transition to type B hydrates. At 5 °C, only type A hydrates were observed due to the lack of driving force to trigger the phase transition.

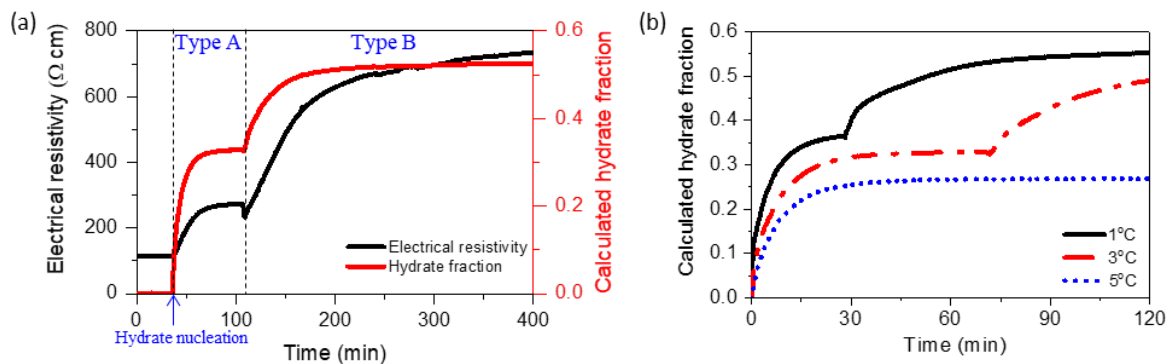


Figure 1. (a) Electrical resistivity and calculated hydrate fraction at 3 °C. (b) calculated hydrate fraction at different temperatures during the hydrate fraction. Time 0 indicates nucleation point.

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Hydrate-like Order Propagation Promotes Nucleation of CH₄ Hydrate in the Presence of Ice: A Molecular Dynamics Study

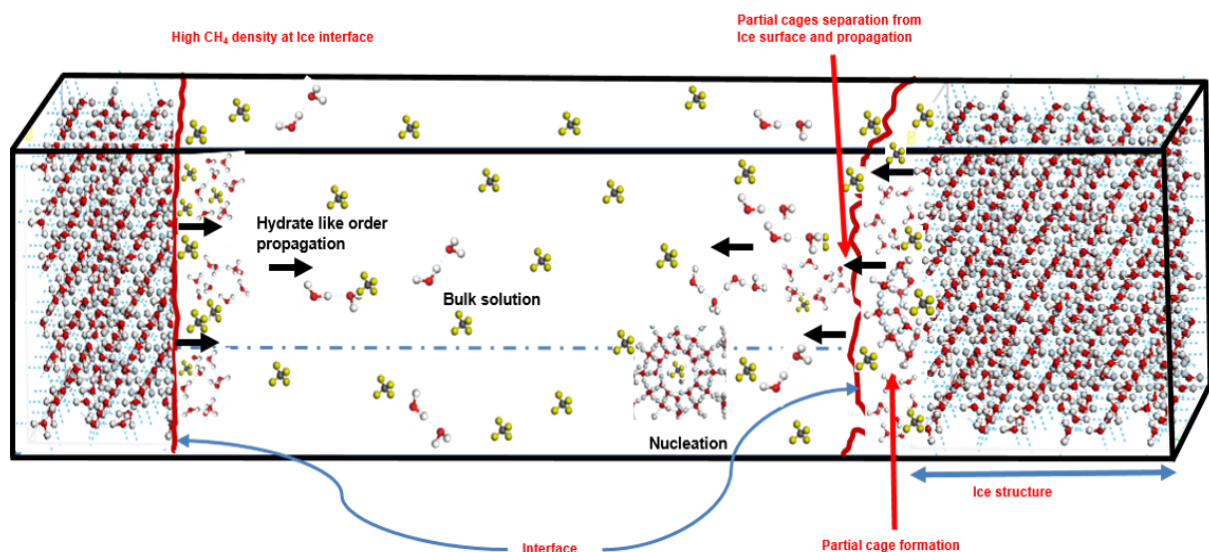
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The heterogeneous nucleation of methane hydrate in the presence of ice (hexagonal ice-Ih) was studied at different initial methane concentrations (from 3 to 10 mole %) at 250 K and 50 MPa using molecular dynamics simulations. The ice growth rate was observed to decrease with CH₄ concentration. The newly grown ice shows stacking faults with formation of layers of hexagonal and cubic ice. The growing ice produced an accumulation of methane molecules near the advancing interface and promoted formation of partial hydrate cages at the ice surface. These partial cages have a short lifetime, but the transient hydrate-like order frequently propagated away from the surface leading to nucleation near but usually not on the surface. A growing ice front thus works as a catalyst-promoting agent and initiates a faster rate of hydrate nucleation compared to the homogeneous system. Under the conditions of the simulation, the nucleation time of methane hydrate was reduced by approximately half in the presence of ice and the catalytic effect of ice has been seen in the form of hydrate order fluctuations from the enhanced ice front. The space-time correlation (Van Hove Function) highlights the diffusional behavior of self and distinct parts of hydrate-like order parameters, which distinguish respectively the roles of molecule diffusion from order propagation through different molecules in the nucleation mechanism. The great majority of runs showed nucleation occurring near the ice interface or in the bulk, while nucleation on the surface was observed only in the cases (4/40) where the growing ice front was cubic.

Keywords: Methane hydrate, quick nucleation, Ice interface, order propagation, surface and bulk nucleation mechanism



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Mechanical behaviour and microstructure of methane hydrate-bearing sandy sediment

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Methane hydrates (MHs) are considered as an alternative energy resource but also a source of geo-hazards and climate change. Physical/mechanical properties of gas hydrate-bearing sandy sediments are strongly dependent on the distribution of hydrates within the pore space. The main interests of this study are to investigate morphologies and pore-habits of MHs formed in sandy sediments at various scales and to study the effects of MHs on the mechanical properties of MHBS. Two MH formation methods were first used to create MHs in sandy sediments at different pore-habits. At the macroscopic scale, MH pore-habits were predicted via comparisons between sonic wave velocities, measured and that calculated based on rock physic models. The effects of MHs formed following the two methods (at different hydrate saturations) on the mechanical properties of MHBS were investigated by triaxial tests. Furthermore, Magnetic Resonance Imaging (MRI) was used to investigate the kinetics of MH formation, MH distribution along with sample height and also MH dissociation following the depressurization method which has been considered as the most economical method for MH production from MHBS. A temperature cycle in undrained conditions was supposed to not only complete MH redistribution in pore space after the water saturation of the sample at high hydrate saturation but also make MHs distributed more homogeneously in the sample even at low hydrate saturation. Furthermore, the mechanical properties of sediments (e.g. stiffness, strength) were found higher at higher MH saturation. At the grain scale, the MH morphologies and pore habits in sandy sediments were observed by X-Ray Computed Tomography and Synchrotron XRCT. Observations (at better spatial and temporal resolution) via Optical Microscopy were finally used to confirm diverse MH morphologies in sandy sediments. Comparisons between observed MH morphologies, pore habits, and existing idealized models were finally discussed.

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Hydrate structural dependency of natural KHIs present in crudes compared to commercial KHI additives

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Kinetic Hydrate Inhibitors (KHIs) have been available on the market now for a number of decades. Although the exact mechanisms by which KHIs inhibit hydrates are not completely understood, modern CGI (crystal growth inhibition) test approaches have allowed the selection of additives that act to prevent or severely limit crystal growth: a property considered more robust than traditional nucleation inhibition (alone) for oil & gas field applications. The CGI procedure is based on evaluating KHIs in the presence of small quantities of hydrates (and/or hydrate 'history') in order to facilitate repeatability, and to test under 'worst case scenario' conditions. From a wide variety of studies using this method, it has been established that KHI failure appears most commonly linked to a sensitivity to structure-I hydrates in (nominally s-II forming) natural gas systems.

More recently, it has been established that some crude oils show clear KHI properties, in that they are able to delay and/or completely inhibit hydrate growth on practical timescales. Here, we report experimental results demonstrating this behaviour for a variety of different oils and laboratory test gases (CH₄, 98% CH₄ / 2% C₂H₆, 85% CH₄ / 15% C₃H₈, and some multicomponent natural gases). Tests with some commercial KHI additives using the same gases with real condensate have also been performed for comparison.

Results show that when crudes display notable natural KHI properties, 'failure' / massive hydrate formation is seemingly governed by the most stable structure-I species present for the gas mix tested. In contrast, for crudes with little to no natural inhibition tendency, hydrate growth is in the form of the most stable structure-II species.

This behaviour is very similar to that seen for commercial additives, confirming that these natural crude oil KHIs are equivalent in action to synthetic KHI polymers. However, the identities of the crude compounds responsible are currently unknown.

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Decomposition studies of CO₂-CH₄ hydrate depressurization process using molecular dynamic simulations

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Abstract:

Depressurization process of CO₂-CH₄ hydrate at nanoscale are investigated via molecular dynamics (MD) simulations using several intermolecular potentials: TIP4P/2005, OPLS and EMP2. MD simulations in NVE and NPT ensembles were performed to investigate the effect of heat transfer to CO₂-CH₄ hydrate depressurization process when the hydrate is connected with gas and liquid separately. MD simulations on the decomposition of CO₂-CH₄ hydrate by depressurization within the pressure range of 0-20MPa indicate that the mass transfer plays an important role in the CO₂-CH₄ hydrate decomposition, and the gas-solid interface is more sensitive to the pressure fluctuation. The moving velocities of interfaces are calculated based the F4 order parameters of different hydrate layers. Also, the Stefan number and Mean Square Displacement (MSD) are calculated and compared to measure the effect of heat and mass transfer process on CO₂-CH₄ hydrate decomposition at different time. According from that, the mechanism is analyzed with the result that the decomposition rate increased and then decreased, due to the influences of heat and mass transfer process.

Keywords: MD simulation; Depressurization; Decomposition; Heat Transfer; Mass Transfer;

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Multiple Recovery and Re-use of Commercial Kinetic Hydrate Inhibitors from Produced Water and Rich Glycol

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Kinetic hydrate inhibitors (KHIs) offer an alternative to traditional thermodynamic hydrate inhibitors (THIs) for the prevention of gas hydrates. KHIs have several advantages over THIs, such as lower required volumes, easier logistics and reduced CAPEX. However, KHIs are once through chemicals leading to increased OPEX, are mostly non-biodegradable and therefore cannot be discharged to sea or disposal wells in fear of aquifer pollution. KHIs can also lead to fouling of process equipment, especially at elevated temperatures.

To resolve these issues, a new KHI polymer removal method using a solvent extraction-based technique has been developed. In this approach, an immiscible extraction fluid is mixed into the KHI containing aqueous phase where the KHI polymer partitions into the extraction fluid, which can then be separated from the aqueous phase. In some cases, the KHI separated this way can be re-used. This process has the potential to solve problems with KHI produced water treatment/disposal, including where KHI is used in combination with MEG, reducing the costs and process fouling and protecting the environment.

A new joint industry project (JIP) is underway with the aim of developing the concept into a commercial process for removal and possible re-use of KHIs upstream of PW treatment or MEG Regeneration systems. The first phase of this project is lab scale evaluation of the solvent extraction method for simulated removal and re-use of two commercial KHI formulations for a real gas-condensate field case. Both the removal efficiency and hydrate inhibition performance of 4 cycles of re-injected/re-used KHI has been successfully demonstrated. Removal of KHI from a real MEG system case was also successfully demonstrated. In the second phase of the JIP, lab scale tests were used to screen extraction and separation equipment and identify optimum process conditions. The upcoming third phase of this JIP is dedicated to demonstrating the selected process concept(s) on pilot scale in a flow loop.

In this proceeding we will give highlights of the early laboratory test results from a produced water case where two field qualified KHIs are removed from PW and reused 4 times, still showing adequate hydrate inhibition performance. Successful pilot tests will confirm the operability of this process in the field.

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Real Time Prediction of Dynamic Hydrate Deposition Trend Using PCA and Recurrent Neural Network with Iterative Transfer Learning

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Preventing the formation of gas hydrate is critical concern in offshore gas and oil production system. There are several models related to predict the hydrate formation concerning its dynamic behavior, however, this empirical approaches have limitation in becoming universally used due to its dependency on geometries and fluid characteristics. Rather than these model-based methods, time series prediction using data-driven methods are gaining popularity. Classical time series models uses statistical methods which cannot applied on the non stationary data or data without patterns. However with deep learning method, prediction of non stationary or abrupt events are possible. Trend of hydrate formation or risk was considered as statistical, which means they have no definite model to describe its behavior. Transition point and sloughing point was predicted to investigate if the models can predict on certain points. Prediction using several kinds of deep learning model, which is designed to make real time prediction using past 60 seconds of time series data was investigated. Dense model, the most basic type among deep learning models, was implemented to demonstrate the prediction ability of deep learning models. GRU(Gated Recurrent Unit) model type was used to handle the sequential time series data. For each models, layer number and dropout rates were varied to find the better model architecture. Higher layer numbers and dropout rate 0.2~0.6 shows best results. Prediction was made on Hydrate risk indicator, which is PCA(Principal Component Analysis) treated sensor data including pressure, temperature, torque and others. Two group of data (200rpm, 600rpm) was used in prediction to examine the universal applicability of the model, showing that training with dataset under similar experimental condition shows better result than training with dataset under different conditions, but its affects less if dataset number gets larger. The results suggested that the deep learning techniques incorporating with time series prediction could be the promising method for hydrate risk management.

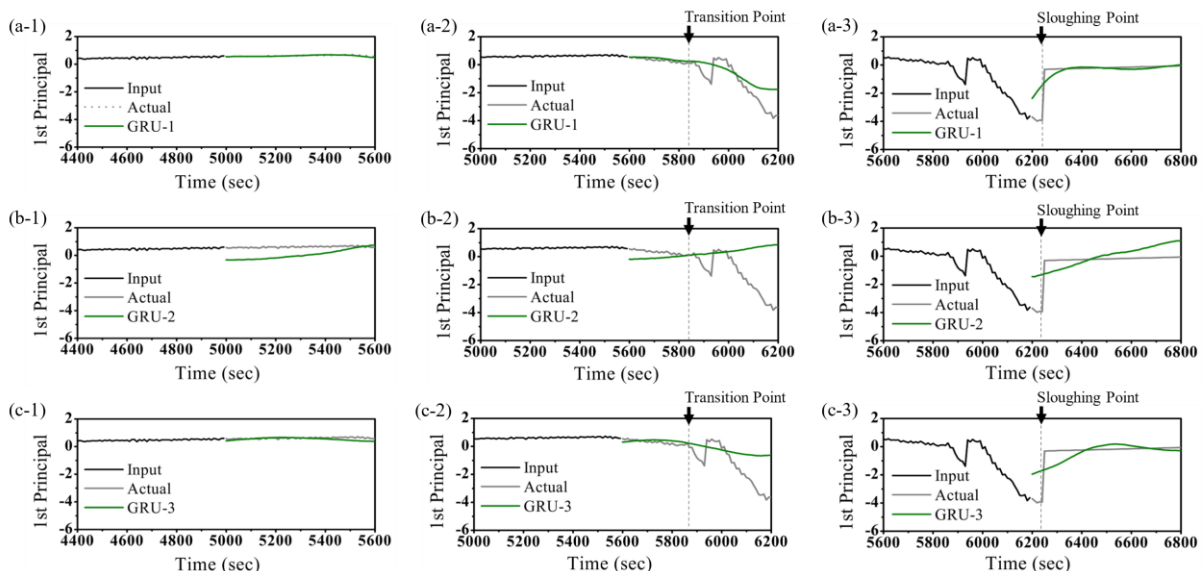


Fig. Prediction results and true values for the test batch (No. 8) of GRU-based model.

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BSRs levels in the west Antarctic Peninsula margin: an inventory of seismic indicators of marine gas hydrates

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In the frame of ICEFLAME project (PID2020-114856RB-I00, Spanish Ministry of Science and Innovation), an inventory of BSRs levels in the west Antarctic Peninsula margin has been carried out. The aim of this inventory is to assess the theoretical transient state of these geological structures due to the global ice-sheet retreat in the Polar Regions. In the west Antarctic Peninsula margin, three areas with characteristic BSR levels have been found: (i) north South Shetland Islands (reported in previous studies), (ii) North Bransfield Island (Bransfield Strait, AP margin), and (iii) Anvers Island (AP margin).

North of the South Shetland Islands, BSR levels had been reported in between the Elephant–King George islands accretionary wedge sector (Lodolo et al., 1993). Two extensive and discontinuous BSR levels (named BSR-1 and BSR-2) have been mapped in the inventory. The BSR-1 appears as local, disconnected and discontinuous patches, about 10 km diameter in geographical extension, of high amplitude reflections of inverse polarity. Its burial depth ranges from ca. 150-200 ms TWT (at the base of the accretionary wedge) to ca. 300 ms TWT (in the middle slope). BSR-2 shows more extensive spatial continuity than BSR-1. BSR-2 levels are well-defined high amplitude reflections of inverse polarity. They simulate the seafloor increasing the burial-depth with water depth from ca. 250 ms TWT in the upper slope to ca. 1s TWT at the base of the accretionary wedge. North off Bransfield Island, BSR levels had been reported in the distal continental shelf of the Antarctic Peninsula margin (Oliveira, 2017). The BSR in this area constitutes a continuous high amplitude reflection of inverse polarity. It shows a shallow and homogeneous burial depth ranging from 145 to 170 ms TWT. South of Anvers Island, a BSR level had been reported to the west of the island in the middle continental shelf of the Antarctic Peninsula margin (Solovyov et al., 2017). Here, the BSR forms an isolated patch of ca. 13 km of extension at a burial depth of ca. 150-200 ms TWT. It shows high amplitude, inverse polarity and a clear cross cutting character.

All of the above BSR levels seem to be in a transient state with respect to their theoretical locations calculated from both pure methane and thermogenic compositions. We put forward two hypothesis for such situation: isostatic rebound and tectonic uplift and/or the presence of overpressured sediments.

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The case study of Electrical field simulating model with the production of Natural Gas hydrate in South China Sea

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The horizontal well pilot production of natural gas hydrate (NGH) was implemented in Shenhu, offshore in the South China Sea in 2020. In the course of production, solid NGH was decomposed into free gas and water, and this phase change might have caused changes in bulk electrical resistivity. However, such changes were not monitored physically in production process, as no such technology is available for hydrate production currently. As for this this changes in resistivity, the diffusive electromagnetic field is sensitive. In this research, a numerical simulation is conducted to understand whether the changes in resistivity can lead to sufficient changes in electromagnetic field before and after production, aiming to find out whether such changes are sensitive enough to be detected with electric field measurements.

Considering the occurrences of gas hydrates, we use a reservoir model with two layers, a solid hydrate layer (45m thick, 8 Ohmm resistivity) on top and a layer of mixed free gas with solid hydrate (25m thick, 10 Ohmm resistivity), respectively, according to the log data. The area with NGH occurrence is set to 100m by 100m. In the simulation, the production process is supposed to have affected a zone in cylinder shape around the well with radius of 30m and thickness of 70m, which is the same as the reservoir thickness. As to the actual production scenario, the zone involved in the production process is composed of mixed free gas and remained NGH. As hydrate saturation is decreased in hydrate production, a resistivity of 5 Ohmm is set to the original hydrate zone after production. As shown in Figure 1A, an electric current source (red dot) at seafloor is used, and the component of horizontal electrical field is computed before and after production. The change is described by the ratio of the difference to the first field while the difference is the two fields shown in Figure 1B. The results obtained indicate that hydrate decomposition is more intensive and the electric field changes more in the portion close to production well, with the maximum value of 1.6. Based on the results obtained, electric field measurements can be applied to monitor the production progress in a NGH reservoir.

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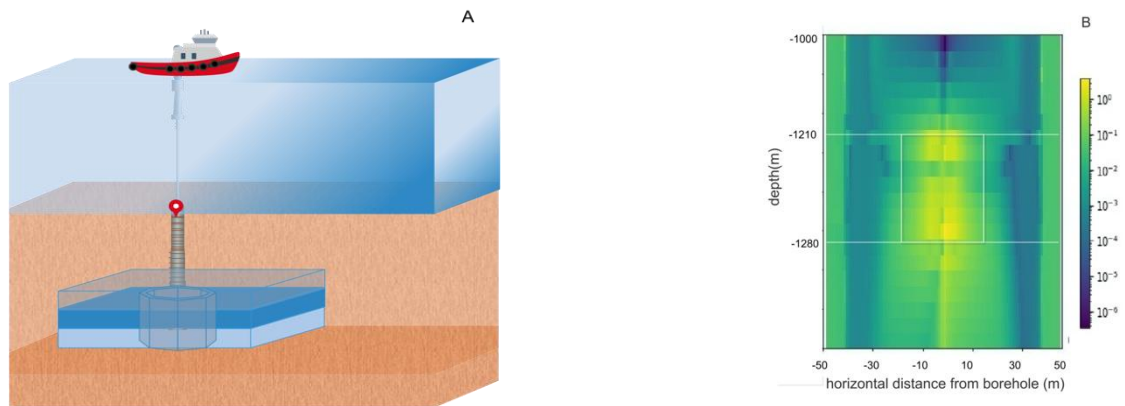


Figure 1 Simulation model (A) and the amplitude of the normalised difference of the electric field before and after production (B). The water depth is 1000 m and the occurrence of gas hydrate is from 200m below seafloor. The cylinder around the well is the production region.

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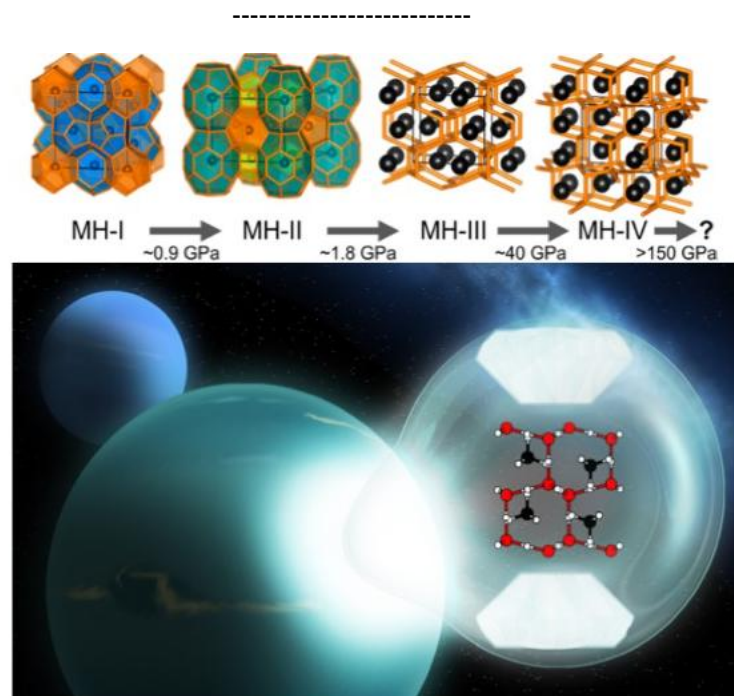
Exploring stability and new structures of H₂, CH₄ - hydrates under planetary conditions

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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 p-T conditions experienced in these medium-size icy bodies, hydrates display a rich phase diagram which has been largely probed in the last decades [4-8]. Methane and hydrogen hydrates are also expected to be present under very high pressures (up to 200 GPa) in giant icy planets interior such as in Uranus or Neptune. However, the stability of hydrates and the new gas rich structures that they adopt at these pressures are currently under study. In this talk I will review our recent experimental results - obtained combining neutron and x-ray diffraction, and Raman spectroscopy under high pressure and ab-initio simulations- on gas (H₂, CH₄) [8,9] filled ices under the extreme conditions experienced in the large ice bodies of our solar system.

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Isopropanol : A hydrate promoter or inhibitor ? Experimental and thermodynamics structural analysis under different concentrations

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In oil exploration and production, isopropanol is a by-product often utilized during well stimulation and workover. In recent years, few studies have investigated its usefulness as a hydrate inhibitor. It has been shown that isopropanol does not provide a significant inhibiting effect like methanol and ethanol. In fact, it takes part in clathrate formation and according to some evidences published in the literature, it may behave as a hydrate promoter under low concentration and high pressure. Due to the scarcity of data and uncertainties regarding the role played by isopropanol in the hydrate formation, experimental evaluations were carried out to assess his inhibition/promotion ability in the formation of methane and carbon dioxide hydrates. The experiments were performed under different isopropanol mass concentrations, ranging from 1 to 2 wt%. Equilibrium data were obtained through isochoric procedure for pressures up to 200 bar. For carbon dioxide systems, isopropanol has been characterized as a hydrate inhibitor. On the other hand, the systems containing methane hydrates displayed a behavior change between the data obtained for 1 and 2 wt%, as can be seen on Figure 1.

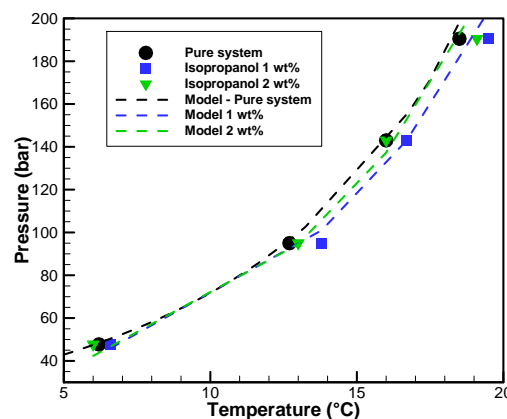


Figure 1. Comparison between the model and experimental data referring to CH₄ hydrates systems in presence of 2-propanol.

In both concentrations it exhibited a promotion effect. However, the 1 wt% aqueous solution presented a greater promotion capacity than the 2 wt% solution. In order to explain this unexpected comportment, a thermodynamic structural analysis was conducted. A model capable of predicting the hydrate formation conditions were developed, coupling the Cubic Plus Association (CPA) equation of state with the van der Waals-Platteeaw theory. To be able to reproduce this behavior through the model, different Kihara parameters were obtained for sI and sII hydrate structures for both gases and isopropanol. The values of core radius were kept constant for sI and sII structures while the distance and energy parameters vary and were calculated using experimental data of hydrate formation conditions. As result, the model were capable to replicate the experimental data behavior and appointed to a structural transition between the hydrates formed in both concentrations of isopropanol.

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In addition to determining the structure formed, the occupancy levels of hydrate cages were also analyzed.

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Phenomenological Analysis of Hydrate Deposition in Non-Emulsified Systems

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Hydrate formation and blockage is one of the concerns in offshore oil and gas production. A solid understanding on the mechanism of hydrate formation and accumulation is the key in order to safely implementing hydrate management strategies. Hydrate formation and accumulation were investigated in three-phase (water, oil and synthetic gas) systems in a high-pressure rock-flow cell with visual capabilities in order to augment the knowledge on the processes leading to hydrate plugging conditions. The experiments were performed in a cylindrical rock-flow cell with an internal diameter of 51 mm and internal length of 500 mm. The rock-flow cell oscillations result in mixing and gravity driven flow. A number of experiments were carried out varying the liquid loading from 40 to 80 vol%, the water cut from 20 to 70 vol%, the rock-flow cell oscillation from 6 to 18.75 rpm to simulate different flow conditions, and the wall temperature from 4 to 10°C to study the influence of wall temperature on hydrate upper wall deposition. The hydrodynamics system proved to be important to understand the morphology of the system in the presence of gas hydrates. These parameters affect the dispersion of the liquid phases influencing on gas-oil-water interfacial area and flow energy, which will give important insight of the lead mechanism associated to hydrate formation and accumulation in multiphase flow. Depending on the experimental conditions, four different hydrate formation processes were identified:

- (1) The flow condition before the beginning of hydrate formation was composed of a layer of dispersed water in oil. At the onset of hydrate formation, hydrate particles were observed flowing in the bulk, eventually the hydrate particles collide with each other, as the rock-flow cell is in constant motion, and because of the capillary effect forms aggregates which can consolidate forming agglomerates of hydrates. At the end, the oil phase flows freely along the rock-flow cell.
- (2) The flow conditions before the beginning of hydrate formation was composed of a thicker dispersed water and oil phase with a thin oil phase above. The liquid phase in the system gradually decreases as the water is converted into hydrates or the oil and water get entrapped inside the hydrate porous structure. At the end, the system dries out, no liquid flow, the oil phase and remained water (unconverted water) were trapped inside the porous hydrate deposits at the bottom of the cell.
- (3) Hydrate particles flowing dispersed in the bulk forming a stabilized dispersed phase (water-oil-hydrate phase) at the beginning of hydrate formation. The constant wetting of the hydrate structure adhered to the wall rapidly increase the deposit forming a thicker hydrate deposits few minutes after the beginning of hydrate formation (approximately < 30 min). A free water phase or oil phase was observed at the end of the experiments.
- (4) At the beginning of hydrate formation, hydrate particles flowing dispersed in the bulk forming a stabilized dispersed phase (water-oil-hydrate phase). As the flow energy was not enough to keep the agglomerate suspended in the flow, eventually they settle down forming a bedding and later depositing in the bottom of the cell. The size of the agglomerate will be a result of capillary effect, shear forces, contact-time and subcooling.

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Stability and metastability of clathrates hydrates with DFT simulations

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Clathrate hydrates mainly crystallize in the cubic structures sI or sII. For some of them, both structures can be observed experimentally. This is the case for CO and N₂ gas hydrates that initially form in the sI structure (kinetically favored) and transform into the sII structure (thermodynamically stable) after a few days (for N₂) or weeks (for CO) [1,2]. Small molecules, such as N₂ or CO, preferentially form the type II structure because of their ability to fill the larger SC proportion in sII when compared to sI. Understanding and predicting the gas hydrate structural stability by investigating the cages occupancy by the guest molecules then becomes of great interest.

The aim of this work is, thereby, to study the structural and energetic properties of the CO and N₂ clathrate hydrates using density functional theory (DFT) calculations. Performed on a complete unit cell (sI and sII), DFT-derived structural calculations based on two different exchange-correlation functionals are compared to experimental data. In addition, an analysis of the DFT potential energies is presented and aims at providing a better understanding of the hydrate structural stability with cage occupancy [3,4].

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Water-Alternating-Gas (WAG) Subsea Injection Manifold : comissioning and operation experience

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The objective of this work is to present the procedures adopted for the commissioning and operation of the WAG subsea injection manifolds (MSIAGs), which operates with simultaneous injection of water and gas, as well as the procedures for exchange of fluids in the 4 platforms that are currently in operation in the Buzios field.

The alternating injection of water and gas (WAG – Water Alternating Gas) in the reservoir is part of the strategy of injection adopted in Buzios field. This strategy guarantees the reinjection of part of the produced gas, reducing CO₂ emissions and optimizing the injection of water into the reservoir, aiming at an increase in the recovery factor of the field.

However, in this recovery method there is an alternation between the injection of gas and water in the manifolds. Therefore, the aspects of flow assurance become extremely relevant and must be carefully analyzed so that, during the fluid exchange operations, there are no hydrate blockages in the system. It is an innovative concept, applied for the first time on pre-salt platforms.

During 2020 and 2021, the 4 platforms in production in the Buzios field commissioned their subsea manifolds for the simultaneous injection of water and gas. The commissioning of this system had as initial state different situations among the platforms. P1 and P3 platforms injected gas into both manifold wells and one of them was then converted to water injection. On the other hand, P2 and P4 platforms were injecting gas into only one of the wells and the other well connected to the manifold

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was commissioned directly for the water injection. There has been no water to gas commissioning up today.

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Influence of thermodynamic inhibitors in interfacial rheology of cyclopentane hydrates

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The deepwater offshore facilities and production lines provide favorable pressure and temperature conditions for the formation of gas hydrates. Hydrate agglomeration can form a plug that block the transportation lines, which can be a big issue for the oil and gas industry, since that it can damage equipment, compromise facility safety, put personnel in safety hazard and harm the marine environment. To prevent or manage the hydrate formation, the industry has been making large investments in the development of processes to ensure regular flow. One method to address this flow assurance challenge is to use thermodynamic inhibitors, such as methanol, salt, and mono-ethylene glycol. The objective of using thermodynamic inhibitors is to change the stable state (“envelope”) of hydrate toward higher pressure or lower temperature to avoid or delay its formation. The process of hydrate formation occurs in two steps: nucleation and growth. Since hydrate nucleation happens at the interface between water and hydrocarbon, it is important to investigate the dynamics of hydrate systems. To this end, interfacial rheology can be a powerful tool to be used. The main goal of the present work is to evaluate the nucleation process of cyclopentane hydrates with and without the addition of a thermodynamic inhibitor. Cyclopentane is used as hydrate former under atmospheric pressure. It forms structure II hydrates, the same as most natural gas systems. This allows the study of hydrate-formation processes without the added experimental difficulties of dealing with elevated pressure. NaCl was used as inhibitor. Oscillatory tests were performed to obtain the rheological response at the interface, using the commercial rheometer DHR-3 (TA Instruments) and the double-wall ring geometry, which is placed at the interface between water and hydrocarbon. To obtain an accurate temperature control of the system, a homemade brass base was employed in the tests. The results are depicted through the interfacial dynamic modulus G' and G'' for different salt concentration. In all cases, hydrate formation is detected by a stochastic growth of the interfacial storage modulus (G') with time. However, with the addition of inhibitor the induction time increases considerably, as expected. After that, G' reaches a plateau meaning that a stable hydrate film was formed.

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Influence of parameters on ethane gas hydrate formation

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In the oil and gas industry there are several challenges in flow assurance. One of the most relevant problems is the formation of hydrates in production lines causing obstruction and damage. Production stopps in this type of industry can cause huge financial losses and environmental concerns. Hydrates are crystalline water-based solids physically similar to ice, formed when guest molecules are trapped inside cages built by the water hydrogen bonds, in conditions of high pressures and low temperatures. Due to these factors, the study of hydrate rheology has become an important factor to be studied both by the industry and academy. There are already methods used by the industry as a way of avoiding or controlling hydrates formation and growth, such as remediation with anti-agglomerant agents and the use of kinetic inhibitors. However, some formations during the production process are so strong that conventional methods can become useless. So, understanding the formation and dissociation of hydrates becomes extremely important. Thus, rheology enters as an important tool to effectively assist in the study of these issues. Due to these factors, the main objective of this work is to perform a rheological analysis of the most important properties of ethane gas hydrate subjected to certain thermodynamic conditions such as high pressures and low temperatures. The rheological study presented was made from water-in-model oil emulsions and the experiments were conducted through a high pressure system composed of a thermostatic bath, Haake Mars III rheometer, high pressure cell and two syringe pump. With the pump used it is possible to quantify how much gas is present during the initial saturation process. The saturation process contemplates the initial 4 hours of the experiments and after that moment the needle valve coupled to the high pressure cell is closed. Then, all tests take place in a closed system, with no gas entering the system after saturation. Results are revealed as a function of the viscosity curve varying with time. The influence of several parameters on the formation of hydrates such as the subcooling degree, the shear rate and the water shear in the emulsion were investigated. When the formation of hydrates was observed, it was possible, through the pressure variation data, to calculate the amount of water that changed state and formed small blocks of hydrates.

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Air - Water Flow in a Rock&Roll Ring Flow Loop: Visualization and Modeling

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Understanding the interdependence between flow morphology and hydrate formation is essential for the safe and efficient transport of multiphase flow systems along pipelines. This work is an initial milestone in the development of experimental and analytical tools for studying the formation and flow of gas hydrates in curved pipes. The scientific problem underlying this effort is whether the methodologies used to solve the horizontal multiphase flow can be extended to the present geometry.

This talk firstly aimed to show the main outcomes of an experimental study of air-water flow under Rock&Roll ring flow loop (Fig. 1a) conditions: flow patterns and flow regime map (Fig. 1b). The results of estimating the volume of air bubbles trapped in the liquid, attained by image processing of flow snap shots will be then discussed. After, an explanation of the idea of energy minimization model¹ is followed. The accuracy of the model evaluated by comparing simulation results with experimental results. Finally, the advantages and future prospects of actual experimental setup for multiphase flow applications will be pointed out.

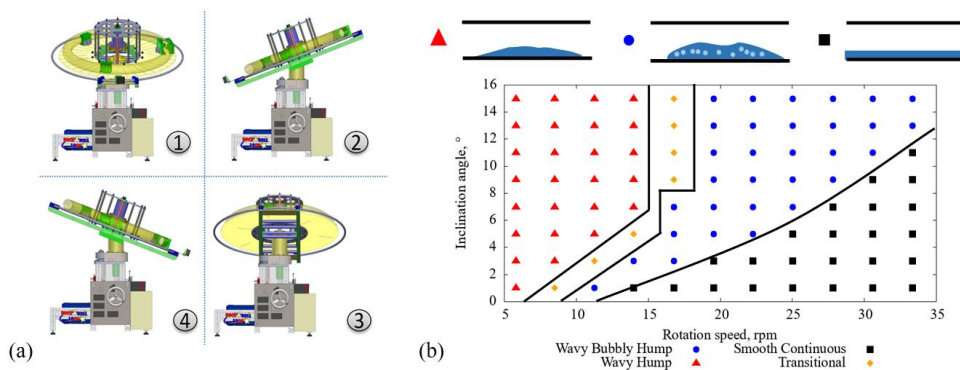


Figure 1 – (a) 3D model of Rock&Roll Ring Flow Loop inclined in four positions, (b) Air-water two phase flow regime map (5% WC, 5° rocking angle)

Clathrate substitution leading to gas generation in Titan subsurface

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Titan, the largest moon of Saturn, has unique surface environments, characterized by a dense atmosphere of N₂ and CH₄ (~1.5 bar) and liquid hydrocarbon cycles. On Titan's surface and subsurface, CH₄ and C₂H₆ clathrate hydrates are thermodynamically stable [1,2]. Upon changes in composition of liquid on Titan throughout time, clathrate substitution might have occurred and influenced Titan's surface evolution [3,4]. Based on molecular dynamics simulation, we previously proposed that substitution of N₂ clathrate, formed on ancient cold Titan [5], by liquid CH₄ and/or C₂H₆. This would cause release of N₂-rich gas, possibly leading to explosions of subsurface materials in north polar regions and formation of deep depression with raised rims [4].

In this study, we aim to estimate timescale of N₂-rich gas generation via clathrate substitution by hydrocarbon fluid. We conducted molecular dynamics simulations for 1) clathrate substitution and 2) gas generation, with GROMACS and molecular models [4]. As for the clathrate substitution simulation, the initial configuration was composed of N₂ clathrate of 2 × 2 × 3 of the unit cell and C₂H₆ liquid of 500 molecules in a small box (3.4×3.4×~10 nm). Simulations were conducted for a few microseconds in Berendsen thermostat and barostat at 3 MPa, corresponding to ~2,000 m in depth on Titan, and at various temperatures of 130–260 K. As for the gas generation simulation, we gradually increased N₂ fraction or temperature in N₂-CH₄/C₂H₆ liquid mixture in a box (3.4×3.4×~5 nm) until the volume increased due to gas generation. Through the simulation, we determined threshold temperature and composition for gas generation at a specific pressure.

As a result of the substitution simulation, we determined activation energy of N₂ diffusion in clathrate as 31±7 kJ/mol from an Arrhenius plot assuming N₂ release from clathrate was controlled by diffusion. This value is comparable to previous experimental results of gas diffusion in clathrate (e.g., 27.3 kJ/mol for CO₂ [6]).

By combining the results of clathrate substitution and gas generation, we calculated timescale for N₂-rich gas explosion through substitution of N₂ clathrate with liquid CH₄ assuming 20% porosity with different clathrate grain sizes at 0.2 MPa (Fig.1). At low temperatures near the surface (~90 K), N₂-rich gas generation would require more than 10⁶ years; whereas, at temperatures of 120 K, corresponding to temperatures at 100 m in depth, N₂-rich gas would be produced in subsurface liquid CH₄ in a short time, from 10¹ to 10⁵ years. On Titan, N₂-rich gas generated in the subsurface could have migrated toward the surface. If there are unpermeable layers in the subsurface, N₂-rich gas might have accumulated, leading to an explosion due to overpressure.

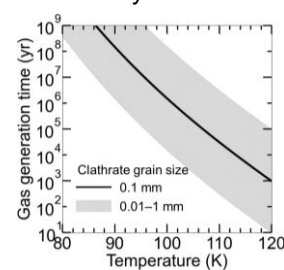


Fig. 1 Gas generation timescales at 0.2 MPa due to N₂ clathrate substitution with pure CH₄ pore fluid with different grain sizes.

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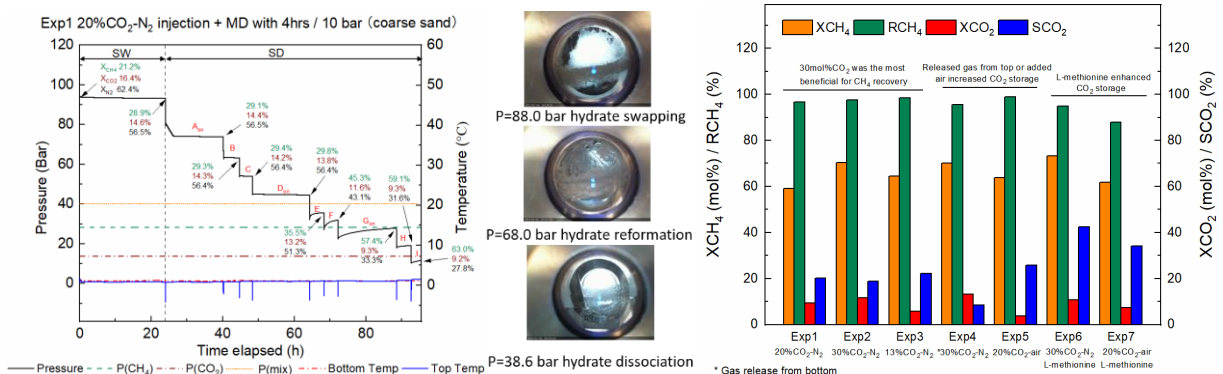
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Characteristics and morphology of CH₄/CO₂/N₂ mixed hydrates using multistep depressurization after hydrate swapping

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Natural gas hydrates are a potentially very large source of energy in the near future. CH₄-CO₂ swapping is a kind of win-win exploitation method to produce CH₄ from hydrate reservoirs while simultaneously storing CO₂. To mitigate the problem of low efficiencies of CH₄ production and CO₂ storage, CH₄-CO₂ swapping combined with depressurization has been investigated intensively. However, few studies focus on multistep depressurization for mixed CH₄/CO₂/N₂ hydrates after swapping. This work presents characteristics and morphology of well-controlled multistep depressurization after CO₂/N₂ or CO₂/air gas injection into CH₄ hydrates, with a view to exploiting this large resource. A high-pressure cell was used to form CH₄ hydrate within unconsolidated sand. Mixed gas of CO₂/N₂ or CO₂/air was then injected into the cell to perform the swapping step. Subsequently, pressure release was conducted in steps to produce gas mixtures. Temperatures at the top and bottom as well as pressure in the cell were recorded. The gas compositions collected from produced gas at each multistep depressurization were analyzed via gas chromatography. The morphology of mixed hydrate dissociation was studied separately in a sapphire cell using same procedures, with temperature, pressure, gas compositions and real-time photos recorded correspondingly. The effects of CO₂ concentration, gas release position, air composition and L-methionine on CH₄ recovery, CO₂ storage and mixed hydrate morphology were comprehensively investigated in the high-pressure cell and the sapphire cell. Three evaluation parameters, i.e. CH₄ or CO₂ mole gas fraction (X_{CH_4} / X_{CO_2}), CH₄ recovery percent (RCH₄) and CO₂ storage ratio (SCO₂) were calculated to quantitatively analyze the exploitation efficiency.



The results from the high-pressure cell showed that 30mol%CO₂ in CO₂/N₂ injection gas was the most beneficial to improve CH₄ concentration. The highest CH₄ concentration was 70.2mol% compared with 13mol% and 20mol% for CO₂. The highest SCO₂ of 18.8% was obtained for gas release from top rather than bottom, while CH₄ recovery efficiencies were almost same regardless of gas release position. The results of SCO₂ and morphology from the sapphire cell indicated that air could increase CO₂ storage by inducing more CO₂-containing hydrate reformation during swapping and multistep depressurization. A similar effect of enhanced CO₂ storage for L-methionine addition was observed in morphology study. The highest SCO₂ of 42.4% was obtained with L-methionine compared to 18.8% without it. In addition, water production was noticed in the morphology experiments when the stepdown pressure was reduced just below mixed hydrate stability pressure. The exploitation results and morphologies in this work confirmed the optimized CO₂ concentration in diluent CO₂-containing gas for multistep depressurization after swapping exploitation. CO₂ storage could be efficiently enhanced by injecting CO₂-air gas or adding L-methionine. The stop point for multistep depressurization should be controlled at pressures just above CO₂ hydrate stability pressure. This investigation shows that high efficiencies of CO₂ storage and CH₄ recovery can be achieved through well-controlled multistep depressurization.

Experimental heat transfer measurement applied to CO₂ hydrate formation kinetic study

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CO₂ hydrate slurry is a promising phase change material for secondary refrigeration cold distribution issues, due to its high latent heat (about 500 kJ.kg⁻¹ of water, higher than that of ice - 333 kJ.kg⁻¹) and wide melting temperature range suitable for air conditioning application. While the thermodynamic properties of CO₂ hydrates are now well established, knowledge of crystallization kinetics phenomena is still a challenge. Trying to understand and control the formation of gas hydrates is a key factor since their discovery in pipeline plugs by Hammerschmidt, but unlike that case, the goal here is to promote the rate of CO₂ hydrate formation. Most laboratory-scale hydrate reactors are equipped with pressure and temperature loggers, and mass balance on CO₂ allows formation kinetic studies, but with assumptions on CO₂ concentration in liquid phase in the liquid phase and the hydration number.

The present work investigates the kinetics of CO₂ hydrate crystallization for different types of stirrers and stirring speed conditions in a jacketed stirred batch reactor. Heat balance obtain experimentally using a specially developed sensor installed on the cooling jacket. The mass fraction of crystallized hydrate determine directly from the heat balance on the cooling jacket. First, tests on water heating and cooling steps and ice crystallization allowed the method validation before to apply it to CO₂ hydrate crystallization. Experimental results described with an empirical model and compared to other mass balance based kinetic determinations. Finally, the development of a simplified thermal model improved this kinetic determination by estimating heat flows inside the reactor and with the environment.

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Grand Canonical Monte Carlo Simulations for modeling gas trapping in Clathrate Hydrates

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Natural clathrate hydrates are conjectured to be present in various extraterrestrial environments like other planets and/or their satellites in the Solar System. In these environments, local conditions could be very different from those usually encountered on Earth leading to the stabilization of clathrates which are never observed there. In addition, specific thermodynamic conditions relevant for extraterrestrial environments may be difficult to reproduce and thus, prevent the laboratory, experimental characterization of these clathrates.

Recently, computer simulations based on an atomic-scale description of the clathrates under consideration have appeared as a promising tool for an accurate characterization of the composition and stability of clathrates, even at low temperature and very low pressures. Molecular dynamics simulations have thus been widely used to investigate clathrates behavior, from their formation to their dissociation. However, such methods usually rely on assumption made on the initial composition of these clathrates. Such assumption may, however, be quite irrelevant with respect to real conditions.

We thus rather performed Monte Carlo simulations in the grand canonical ensemble, because the number of enclathrated molecules is allowed to vary in the calculations, as a function of the pressure. This method thus allows the direct simulation of the trapping isotherms, for both pure and mixed clathrates, i.e., systems that are in contact with a fluid phase containing either one species only [1,2], or a mixture of different species with given compositions [2,3,4].

Here, we specifically focus on our newest results, obtained on the CH₄/C₂H₆ and CO₂/O₂ mixed clathrates, and also on the pure OCS clathrate.

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Hydrogen-rich Natural gas Hydrates Formation Kinetics

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2

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Keywords: Hydrogen Storage, Promoters, Formation Kinetics

*Speaker

Modeling CO₂ solubility in DESs using Cubic Plus Association and Peng-Robinson Equations of State

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The increasing global levels of greenhouse gases (GHGs), especially CO₂, have caused environmental problems that impact the humanity and ecosystems [1]. CO₂ capture and storage (CCS) has become one of the effective methods to prevent the release of large quantities of CO₂ into the atmosphere [2]. Among several technologies for CO₂ capture, aqueous amine solutions, such as monoethanolamine (MEA), have traditionally been used as chemical solvents to CO₂ capture. However, they are not eco-friendly due to their toxicity, corrosive byproduct formation, and high uptake costs. Thus, scientists and engineers have developed economic absorbers [3,4] such as deep eutectic solvents (DESs) for replacing MEA [5,6].

Over the years, several studies have been carried out to experimentally determine the CO₂ solubility in DESs [7,8]. Not less important, thermodynamic modelling provides knowledge about the system behavior, nevertheless studies in which experimental data of DESs + CO₂ are modeled are still scarce in the literature, especially those using Cubic Plus Association equation of state (CPA EoS). This research seeks to use CPA and Peng-Robinson 78 (PR78) EoSs to describe the behavior of binary mixtures found in literature formed by DES (tetrabutylphosphonium bromide (TBPB) + diethylene glycol (DEG) at 1:4 molar ratio and choline chloride (ChCl) + glycerol (GL) at 1:2 molar ratio) and CO₂. It was considered two approaches, DES as a mixture of components (individual) and as pseudo-component.

Figure 1(A) compares PR78 and CPA results in their best configuration, i.e., with fitted binary interaction parameter for TBPB + DEG at 1:4 molar ratio and 313.15 K. Although both models predict well the CO₂ solubility in DES, PR78 showed better results than CPA due to its smaller deviation (9.53% for PR78 and 20.52% for CPA) — an expected outcome, given that CPA is far more complex than PR78 EoS, thus making it a good fit for modelling CO₂ solubility in DESs.

Figure 1(B) compares the pseudo-component and the individual approaches for ChCl + GL at 1:2 molar ratio and 313.15 K. It is possible to observe that individual component is better than the pseudo-component approach, as the deviation is smallest. As DESs are not a pseudo-component, but rather a mixture of two or more components, the individual component approach is expected to predict experimental data better than the pseudo-component one.

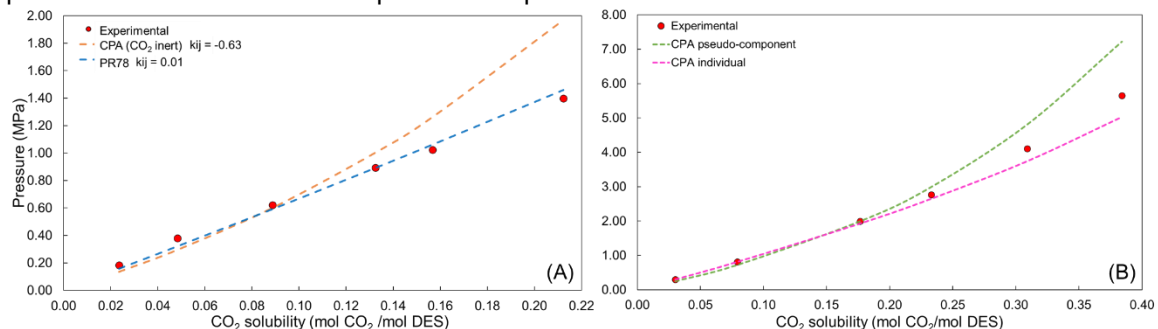


Figure 1. Comparison between CO₂ solubility by CPA and PR78 EoS in: (A) TBPB + DEG at 1:4 molar ratio and 313.15 K and (B) ChCl + GL at 1:2 molar ratio and 313.15 K considering pseudo-component and individual component approaches.

The results show that both EoSs are suitable for modelling CO₂ solubility in DESs, however the deviation was smaller when PR78 was used. Moreover, CPA presents better results to individual component approach instead of pseudo-component one.— for DES are considered a mixture of components rather than.

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Prediction of gas solubility in Deep Eutectic Solvents using COSMO-RS as a tool

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Carbon Dioxide (CO₂) is the greenhouse gas that most contributes to global warming and climate change due to fossil fuels combustion, transportation, and other industrial processes [1]. Carbon capture, storage, and utilization (CCSU) is an effective method to reduce CO₂ emission [2]. Monoethanolamine (MEA) has been proved to be the most efficient chemical solvent to absorb CO₂, but it is not eco-friendly. Consequently to develop new capture technologies, as novel processes and the use of new solvents such as Deep Eutectic Solvents (DESs) to CCSU, is the key point to CO₂ capture [3].

Over the years, several studies sought to determine the solubility of CO₂ in different DESs by experimental techniques, considering distinct HBAs and HBDs, molar ratio, temperature, and pressure range [4,5]. Nevertheless, several possible DESs can be formed which makes difficult to identify the best DESs for CO₂ capture based on the experimental measurements only. Therefore, it is needed a screening method that quickly and reliably predicts the CO₂ absorption capacity in DESs. COSMO-RS seems to be a tool able to predict the CO₂ solubility in DESs and this kind of study is still scarce [6,7]. This research seek to predict the CO₂ solubilities in 2 DESs formed by choline chloride (ChCl) + ethylene glycol (EG) and ChCl + glycerol (GL) both at 1:2 molar ratio and 303.15 K with COSMO-RS and compare the results with the experimental data found in literature.

Figure 1 shows the comparison between the CO₂ solubility in DESs obtained experimentally and its prediction using COSMO-RS. It is possible to observe that in both cases COSMO-RS could predict the CO₂ solubility very well with a root mean square deviation (RMSD) equals to 0.18% for ChCl + EG and 0.64% for ChCl + GL. The pressure increase leads to a higher RMSD for both cases. The prediction underestimates the experimental CO₂ solubility data of ChCl + EG system (Figure 1A) and overestimated the solubility of ChCl + GL (Figure 1B) due to totally predictive characteristic of COSMO-RS model.

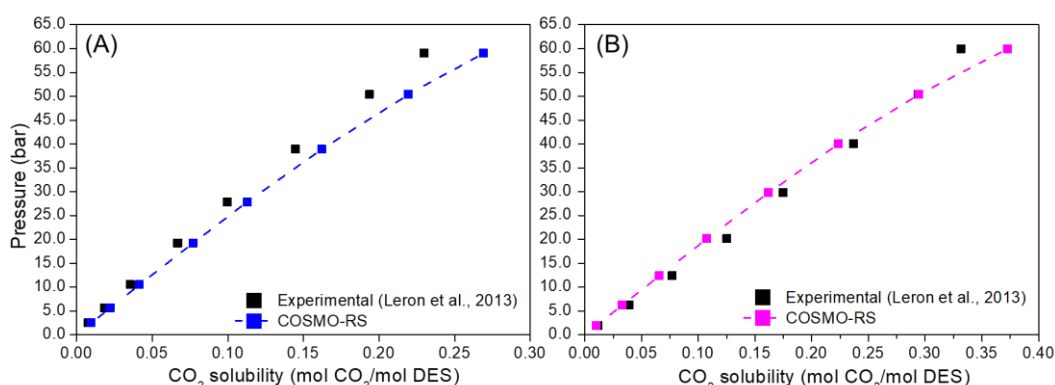


Figure 1. Comparison between experimental data of CO₂ solubility in DES [8,9] and modelled data by COSMO-RS for (A) ChCl + EG and (B) ChCl + GL both at 1:2 molar ratio and 303.15 K.

The results indicated that COSMO-RS can satisfactorily predict the solubility of CO₂ in the studied DESs with RMSD smaller than 0.65%, which shows that COSMO-RS could anticipate experimental data and it is a reliable tool for DESs screening.

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Ethanol substitution by MEG as hydrate inhibitor on gas lines

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In every Petrobras platform ethanol has been used as hydrate inhibitor for several years. A demand to assess alternatives to ethanol usage came up due to a process security review and monoethylene glycol (MEG) was pointed out as the best alternative. Since MEG has higher viscosity than ethanol and is more prone to stay on liquid phase, which would result in pressure increase, it was necessary to evaluate if well production and gas exportation would be affected by MEG injection in the gas currents.

Steady-state and transient flow simulations were performed to evaluate the equilibrium condition as MEG replaced ethanol and, most importantly, how that equilibrium would be reached in gas exportation networks (3 independent networks linking 12 oil producing platforms) as pressure increase was expected, but the rate at which the exportation pressure would raise was unknown.

The simulations considered worst case scenarios. The gas flow rate and pressure at the importation node data was compiled on daily average basis and the maximum values were considered. Most steady-state simulations showed a significant pressure increase, except for platforms with high gas exportation flow rate.

Therefore, transient simulations were performed to evaluate the rate at which pressure increased at five MEG injection flow rates: 300, 600, 1000, 1500 and 2000 liters per day. As expected, the results indicated that higher MEG flow rates resulted in faster pressure increase. There also could be noticed that geometry, the network parameters, and fluid composition were very influential on the results.

The main result was that MEG injection could be considered possible in all platforms, even in the ones with low gas exportation flow rates. The expected exportation pressure increase rate was 3 bar/month or less, and the pigging routine should be able to remove any additional liquid added by MEG, resetting the pressure to normal standards.

Simulations also indicated that momentarily increasing the gas exportation flow rate should enable the gas flow to carry additional liquid stored in the gas pipeline, hence lowering the system pressure.

During the study, it was detected that evaluating the effect of MEG injection on gas lift ring and subsea chokes was also necessary. Since it's not possible to perform a pig cleanup on the gas lift ring, an eventual liquid load effect could be dangerous. However, simulations results showed that the downward flow and the smaller diameter on the ring favored liquid carrying and, even on extreme scenarios, halting MEG injection was enough to nullify the pressure increase.

Regarding the subsea chokes, it was noticed that some flow restrictions may cause fluid temperature to drop near or even below -15 °C. Since MEG's melting point (-15.6°C) is way higher than ethanol's (-114°C), there was the possibility of MEG particles becoming solid and cause a blockage in the line. It was concluded that a solid blockage was not expected, especially because MEG's flow rate is much lower than gas flow rate, which would result in eventual MEG solid crystals being dragged by the gas.

Currently at least 6 platforms replaced ethanol by MEG. All of them reported no noticeable changes on exportation pressure and three even reported fewer hydrate cases on gas lift lines.

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Practical decisions regarding reservoir hydrate risk mitigation in pre-salt projects

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The Water Alternating Gas (WAG) injection as an enhanced oil recovery (EOR) method applied in the development of the pre-salt fields in Brazil. Besides the predicted production increase, this injection helps the gas to match the specifications needed to be exported and commercialized, as these fields have a high CO₂ content in the fluid. After the gas treatment at the platform, a tailing stream with a CO₂ content higher than the original composition is generated, thus the injection of this gas is a guideline to meet the policy of reduction greenhouse gas emission. Therefore, the WAG injection comes up as a solution to deal with this CO₂ excess, also helping to increase the fields recovery factor.

In most production areas, the WAG injection is performed without major operational problems. However, as new projects are considering the use of rigid lines with a small thermal insulation, instead of the conventional flexible lines due to corrosion problems, and process plants with a lower than usual water injection temperature, conditions for this operation have changed and a new risk of reservoir hydrate formation has arisen. The critical area for this phenomenon is around the injection well, and its occurrence and possible effect is still a matter of great discussions.

Combining thermohydraulic flow simulation results and a reservoir thermal simulation, this study investigated the temperature behavior in the well's surrounding along time, following the low temperature injection cycles of water and gas. The results show that there is a real possibility of hydrate formation in the reservoir, especially after fluid swap, which may decrease the permeability and the well injectivity. This reduction has the potential to negatively impact the reservoir mass balance, which leads to a lower oil recovery factor in the project.

Thereby, projects that intend to use WAG injection as an EOR method should evaluate the need of thermal insulation in the injection lines and the minimum temperature for fluid injection, in order to avoid operation inside the hydrate region at the reservoir condition during the entire production life.

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Cohesion in Methane Hydrate-Bearing Soil; *To Be or Not To Be?*

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Natural methane hydrate reservoirs are gaining worldwide attention due to the abundance of methane hydrate in nature. The geomechanical study in methane hydrate-bearing sediments (MHBS) addresses topics such as subsea landslides and gas-production wellbore collapse. In general, a geomechanical study describes the mechanical behavior of soils as they relate to strength, stiffness, dilation, and other phenomena. A dominant factor in the MHBS mechanical behavior is the sediment strength, which is associated with friction and cohesive properties. While there is a robust scientific agreement concerning the MHBS friction description, there is no consensus regarding the role of cohesion in MHBS behavior. This paper discusses this disagreement in terms of experimental interpretations, different modeling approaches, and the pore-space hydrate morphology, that have been presented in previous works. The paper shows that contrary to the physical property of cementation, cohesion is a model-related parameter and, as such, can only be studied in the context of the considered geomechanical model.

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Demonstrating CO₂ hydrate stability in oceanic sediments on lab scale to promote CO₂ sequestration

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Increase in CO₂ emissions in the atmosphere after the industrial revolution has proven to be a global problem, resulting in climate change and other difficulties such as rising sea levels, melting Arctic ice sheets, flooding, and the emergence of a range of diseases that are damaging to human health. The majority of these emissions are due to the transportation and industry sector. In 2021, global CO₂ emissions were anticipated to reach 36.4 GtCO₂. The United Nations Climate Conference COP26 Glasgow [2021] placed a heavy emphasis on formulating action plans to meet the Paris Agreement's [2015] objective of a carbon-free economy by 2050. Carbon Capture and Storage [CCS] is widely recognized as a vital approach for attaining the goal of a zero-carbon economy.

Compressing captured CO₂ to the liquid phase and injecting it into the deep ocean sediments is an emerging approach to storing CO₂ in areas without good geologic storage capacity. Because direct disposal of the liquid CO₂ into the ocean floor is problematic, it's more viable to store liquid CO₂ as hydrates within the oceanic sediments. Gas hydrates are crystalline compounds that are formed when small CO₂ molecules are trapped within water molecules at high pressure and low-temperature conditions. One unit of gas hydrate can store up to 184 units of gas at STP. However, the key concern is the stability of these hydrates in oceanic sediments.

In this work, stability of the CO₂ hydrates was evaluated across oceanic sediments by synthesizing an artificial sand bed inside a high-pressure reactor system. In stage 1, the hydrates were formed across the sea bed using multiple pressurizations. In stage 2, these hydrates were submerged in a water table for 14-30 days and their stability was monitored continuously using the top and front-mounted cameras at high pressure [10 MPa] and low temperature [4 oC] conditions found at depth of 1 km in the deep ocean. The hydrates demonstrated a decent level of stability throughout the 14-30 days of the test. In stage 3, an intentional depressurization-heating test further confirmed the presence of a significant amount of hydrates inside the sand bed. This indicates that the hydrates inside the sand bed are likely to be more stable than the ones at the surface of the sand bed.

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Energetics of mixed carbon dioxide and methane hydrate clathrates

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Environmental and energetic demands require an atomic level insight into the processes that yield to carbon dioxide sequestration and methane release in clathrate hydrates of these two gases. Based on first-principles density functional theory calculations, we carry out an investigation of the thermochemistry associated with the progressive occupation with single methane and carbon dioxide molecules of the two types of cages present in the low pressure *sI* clathrate structure (H, left, and P, right, see Fig. 1). The average computed enthalpy for methane occupation is around 5.75 kcal/mol regardless the shape of the cage, whereas carbon dioxide displays a greater preference for the H cage (6 kcal/mol) with respect to the P one (4.6 kcal/mol). Overall, the saturation process yields to a similar stabilization of the gas hydrate, around 47 kcal/mol, for both methane and carbon dioxide with respect to the empty structure and the gaseous molecules. Other interesting outcome of our study reflects how methane molecules do not see each other when are progressively encapsulated inside the water framework. This is in contrast with carbon dioxide *sI* clathrate that shows a wider range of enthalpy values for a single occupation of the same type of cage as saturation progresses. Our results allow to derive a simple yet reliable model to recreate the energetics of mixed methane-carbon dioxide clathrate hydrates by linear interpolating energy values and structural parameters obtained in the two isolated gas structures. To verify the plausibility of this versatile model and correct potential deviations, accurate calculations in selected $(\text{CO}_2)_{8-x}(\text{CH}_4)_x @ sI\text{-H}_2\text{O}$ crystals are proposed. Our results will be contrasted with recent theoretical values and available experimental data.

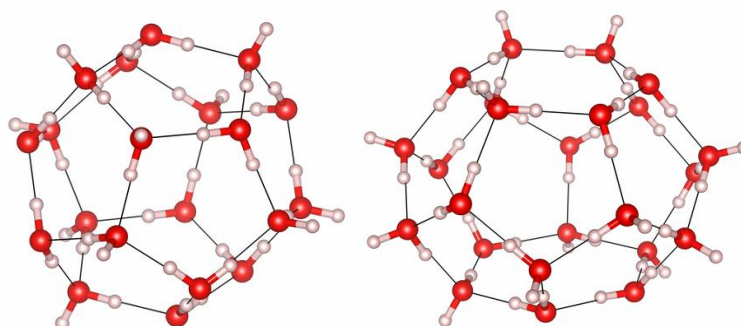


Fig. 1. P (left) and H (right) types of cages in the *sI* gas clathrate structure. O is shown in red and H is in white

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Probing selectivity and capture process in carbon dioxide-based gas hydrate: investigation by Raman spectroscopy

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Combustion exhausts contain mixtures of N₂, CO₂, CO, H₂O and O₂, where CO₂ and N₂ can represent the main components with a typical CO₂ concentration of 15% in power plants. According to the IPCC Special Report on CO₂ carbon storage, more than 60% of carbon dioxide emissions in the atmosphere originate from power plants activity [1]. Gas hydrates are being regarded as a novel CO₂ capture and storage (CCS) technology for reducing CO₂ emissions to alleviate the influence of global warming. They present obvious advantages in comparison to conventional chemical solvent absorption technology (amine): a simple process, moderate operation conditions, continuous operation, a recyclable working medium, and a capture process with no contaminants. Gas hydrate formation has been recently proposed as a potential strategy to separate carbon dioxide from combustion flue- gas [2]. However, the proposal of exploiting gas hydrate properties to carry out the selective removal of CO₂ from a gaseous mixture containing different compounds still presents a margin of improvement, specifically in terms of energy saving [3], selectivity [4,5], and capture [6].

The metrics of performance parameters in gas separation using hydrate technology rely on different parameters that are related to equilibrium thermodynamics and hydrate formation kinetics. In the present study, we show how Raman spectroscopy can be applied to derive quantitative parameters on structure, selectivity, and recovery fraction in gas separation processes involving carbon dioxide molecules. Furthermore, kinetic parameters related to the normalized gas uptake $\Delta n_{g,t}/n_{H_2O}$ [7] and hydrate growth rate $\Delta n_{CO_2,t}/V_{H_2O}t$ [8] are derived to evaluate the influence of promoters on the kinetic of the separation process using hydrates.

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Methane recovery and carbon dioxide disposal in natural gas hydrate reservoirs: experimental results of an Italian research project

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The present paper presents the results obtained by the University of Perugia (UNIPG) in a three-year national research project on natural gas hydrate exploitation, still ongoing. The partners' consortium is led by UNIPG, which includes the Applied Physics group (PI Federico Rossi) and the Structural Geology group. The other partners are University of Camerino (UNICAM), Politecnico di Torino (POLITO), Istituto di Oceanografia e Geofisica Sperimentale (OGS) and University of Ferrara (UNIFE).

The proposed project aims to develop an innovative technological solution for the extraction of methane from marine natural gas hydrates (NGH) and the simultaneous sequestration of carbon dioxide in a single process. The obtained fuel is neutral in terms of climate changing emissions and therefore equivalent to renewable energy sources. The multidisciplinary expertise of the consortium is organized to pursue five specific objectives:

1. Analysis of marine hydrate reservoirs, potentiality and infrastructures for their exploitation
2. In-lab reproduction of hydrate sediments and determination of kinetic and thermodynamic parameters
3. CO₂ replacement in methane hydrates
4. Development of a scalable technology for CO₂ injection/CH₄ extraction in natural hydrate reservoirs
5. Theoretical model applicable of marine hydrate reservoir and energy/environmental evaluations on the proposed process.

The first three objectives are devoted to obtain a body of knowledge on the chemical, physical and geotechnical properties of marine NGH and on the CH₄-CO₂ replacement mechanism. For the activities in these three objectives, laboratory facilities of UNIPG and UNICAM are used. In addition, laboratory facilities of "D'Annunzio" University of Chieti-Pescara (UNICH) are employed since UNICH has available a patented reactor to study the kinetics of the hydrate formation process.

Objective 4 concerns the design and construction of a scalable device for methane extraction and CO₂ replacement. It is integrated with a methane purification and CO₂ recirculation section and tested in a seafloor simulator, where water-rich NGH sediment reproduction and in-situ measurements will be performed. Finally the last objective focuses on the development of a theoretical geophysical model of the marine NGH reservoir and final evaluations on energy, environmental and economic impact of the proposed process and technological solution.

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High-efficiency hydrogen storage by clathrate hydrates

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The present paper proposes a new methodology for hydrogen (H₂) storage reducing energy costs, loosening technical boundaries and providing safety and reliability.

The proposed methodology exploits Clathrate Hydrates (CH) which, under proper conditions, host H₂ molecules. The process is boosted by complementary reusable gases which facilitate H₂ diffusion and stability into CH and reduce energy required to store and release H₂.

CH are solid crystalline compounds which form under proper pressure and temperature values: water molecules produce an ice-like crystalline structure around the gas molecules (guests). H₂ is a hydrate-forming gas. H₂ CH are intriguing and feasible materials for H₂ storage due to their appealing properties such as high safety, reliability and low costs.

The research will pursue a cost-effective, safe and stable H₂ storage by using H₂-based binary mixtures (H₂ with CO₂, ethane, propane and butane as aid-gases) and ternary mixtures (H₂/CO₂/hydrocarbons). So, H₂ separation from aid gases is required and also investigated.

The expected H₂ storage results are: capacity up to 30 vol%, storage energy below 5MJ/kg at 35bar, 2°C. Such data are extremely competitive with traditional storage technologies. The research will strongly contribute to promote the European strategy on H₂, which estimates the production of green H₂ as 10 Mtons by 2030. This strategy results in a huge amount of energy needed for storage. The hydrate-based storage addresses this issue producing an estimated reduction on energy needs for H₂ storage of 50% with respect to traditional methods introducing also safer and more reliable conditions.

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Study of Hydrate/Waxes Deposit's in Presence of AA-LDHI

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Hydrate management remains a major concern in Oil and Gas industries. Nowadays Flow Assurance studies consider more and more complex systems due to harsher conditions of news discoveries. The use of AA-LDHI (anti-agglomerants or hydrates dispersants) is more and more considered as a robust alternative to MEG loop for gas condensate fields hydrate management. The possibility to use AA-LDHI with a waxy condensate exists but the interactions between hydrates (in presence of AA) and waxes are not yet well known.

The paper presents laboratory results exploring such systems. An original high-pressure deposit plate device was inserted in a high-pressure hydrate cell equipped with a special stirring device. The temperature of the deposit device was fixed independently from the environmental temperature in the cell bulk. The temperature difference allowed the waxes' deposit formation. This deposit has been done in presence or in absence of hydrates. The cell was equipped with sapphire windows which allows the deposit thickness's visualization.

After hydrate formation and wax/hydrate deposit growth visualization, the hydrates were dissociated in static cold conditions. The pressure and temperature were adapted to melt hydrate without forming ice but at sufficient low temperature to avoid wax deposit melting. The cell was then opened, and the deposit was sampled and analyzed using atmospheric DSC calorimeter.

Without AA-LDHI and outside the hydrate stability zone, wax deposit was observed on the cold plate. Without AA-LDHI and with hydrates surprisingly no deposit was seen may be because the bulk system presented a sorbet consistency. With AA-LDHI, flowable mixed suspensions of waxes and hydrates were formed. These suspensions are probably transportable. However, with the procedure applied, the presence of AA-LDHI didn't avoid deposit formation on the cold plate and significant deposits were observed. After hydrates dissociation, the deposit's composition analysis exhibits either waxes and hydrates co-deposition or waxes then hydrates deposition. Deposition mechanism seems to be linked to the wax's population (nature and quantity) and not to the AA-LDHI additive

Key words: Anti-agglomerant, hydrate, wax

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CO₂ storage in depleted reservoir: a methodology to assess hydrates risk in the near wellbore area

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Climate change and mitigation of global warming require limitation of anthropogenic CO₂ content in the atmosphere. One proposed method to control CO₂ increase is its geo-sequestration (CGS) into depleted reservoirs. The storage resource of a reservoir is linked to the associated wells injectivity mainly in the near wellbore zones. The formation of CO₂ hydrates due to CO₂ injection and the associated thermodynamic phenomena may greatly alter the petrophysical properties of these zones. This adiabatic depletion leads to a large temperature decrease which can bring the system into the CO₂ hydrates stability zone in the near wellbore area. If those conditions are encountered, loss of injectivity can be anticipated due to CO₂ hydrate formation, plugging partially or totally the pore throats. Rather few results are available on the CO₂ hydrates formation in these peculiar conditions of depleted near wellbore region.

Loss of injectivity due to hydrate formation's risk is addressed in an integrated study including: thermodynamic measurements and comparison with models, hydrates formation in porous media in static conditions (20 MHz low field NMR) and finally hydrate formation in porous media in dynamic conditions (CAL-X experimental set-up). Measurements of hydrates stability zone in the bulk systems, depending on the water salt composition (wide range of concentration) have been performed and comparison with thermodynamic commercial models have been done. The hydrate formation in porous media is on-going. The first porous media chosen is a (high permeability) clay-free sandstone.

In static conditions after setting the system at a targeted water saturation (10 to 50%), experiments are conducted in an in-house high-pressure NMR set-up including a Peltier cooled probe. Taking advantage of the huge relaxation contrast between protons part of water molecules and hydrates, the average water content can be measured continuously during hydrate formation and dissociation as well as water profiles along the sample. The capacity of the Peltier cooled NMR system to accurately control the temperature including ramps as low as 0.1°C/h allows a determination of the thermodynamic stability limits.

Effect of hydrate formation on alteration of the permeability of porous media is also investigated. For this purpose, a series of high-throughput X-ray monitored coreflood experiments is conducted using a state-of-the-art equipment (CAL-X). Experiments are performed under a constant flow rate of CO₂ at different initial water saturations. During CO₂ injection, water saturation as well as hydrate formation/dissociation are monitored by time-resolved X-ray radiography. The measurement of the pressure-drop across the sample during

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hydrate formation is used to evaluate the extent of the permeability change. It is observed that the higher the initial saturation, the greater the alteration of the permeability.

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Modelling of the phases of burial-driven gas hydrate and methane gas re-cycling

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Gas hydrate recycling is an important process in natural hydrate systems worldwide. The recycling of hydrates often leads to high hydrate saturation close to the base of the gas hydrate stability zone (GHSZ). However, to date it remains enigmatic how free gas is recycled back into the GHSZ and what the controlling factors are. Here we use a 1D compositional multi-phase flow model to investigate the dominant mechanisms that control natural gas hydrate recycling. As case study, we apply the numerical model to study hydrate recycling at the Green Canyon Site 955 in the Gulf of Mexico, where high sedimentation rates are thought to drive vigorous hydrate dissociation and re-invasion of free gas into the stability zone. Our novel results suggest that hydrate recycling is a highly dynamic process in which hydrates form and dissociate at surprisingly rapid rates with an inherent cyclicality. These cycles can be divided into three phases of 1) gas accumulation phase, 2) gas breakthrough phase and 3) uninhibited hydrate build-up phase presented in Figure 1. During the first phase hydrates are dissociating and free gas accumulates below. After the free gas saturation reaches a threshold value (given by the mutual effects of entry pressure, bulk permeability, and relative permeability function), gas breaks through the barrier of the remaining hydrate layer. Controlled by permeability and kinetic rate a new hydrate layer forms. In the absence of external perturbations to the GHSZ, gas migration leads to a distinct hydrate layer with a convex distribution of hydrate saturation. Such a hydrate layer acts like a converging-diverging 'nozzle' for the gas flow, when gas enters the hydrate layer, it decelerates until it reaches the peak hydrate saturation (i.e. the nozzle throat), and then accelerates until it exits the hydrate layer on the other side. This nozzling effect, together with the hydrate dissociation kinetics, leads to the cyclic behavior of hydrate recycling. We suggest that the evident cyclicality of burial-driven gas hydrate build-up process provides a new advanced understanding of natural gas hydrate recycling process, and free gas invasion mechanisms into the GHSZ.

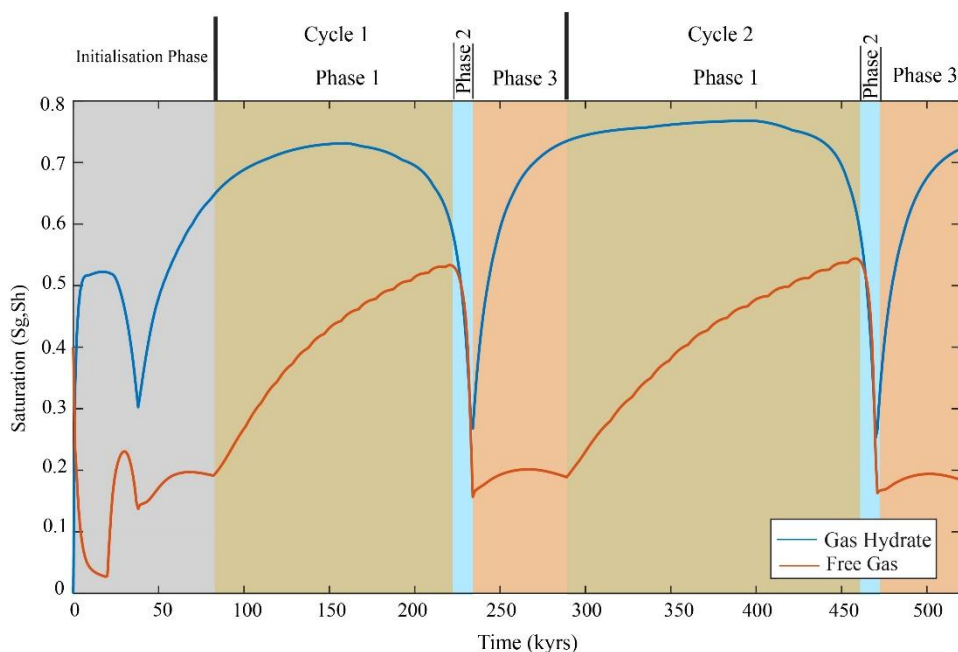


Fig. 1. Three distinct phases (brown, blue, and orange fields, respectively) of gas hydrate (blue line) and free gas (red line) recycling at the base of the GHSZ (Schmidt et al., accepted).

PHASE EQUILIBRIUM FOR SEAWASTE WATER TREATMENT AND CARBON CAPTURE WITH CLATHRATE HYDRATES

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New hydrate-based processes combining different applications are now a topical subject in the hydrate community. This effort focusses on carbon capture as well as desalination or water treatment. Here, carbon dioxide can be considered as a guest that will be captured as well as the hydrate promoter that will separate water from brine. In addition, cyclopentane is an interesting co-former since it presents a very low solubility in water, and promotes significantly the hydrate formation.

Efforts have been made in order to furnish thermodynamic data and models for mixed cyclopentane/carbon dioxide hydrates in presence of salts (NaCl+KCl, MgCl₂, CaCl₂). Results have been obtained in a pressurized batch reactor within a pressure range of 10-25 bars and salinity up to 10% mass (fig. 1). Final dissociation points and as well as intermediate metastable points were obtained. The dissociation enthalpies and compressibility factors have been calculated and compared to literature data. Furthermore, the thermodynamic consistency of our results and literature data were performed to discuss their reliability.

Finally, results have been modelled and compared according to van der Waals and Platteeuw model (vdW-P), Hu-Lee-Sum (HLS) correlation, and ice melting point method derived from HLS proposition. Simulations furnishes temperature data within 0.9 K difference (fig. 1).

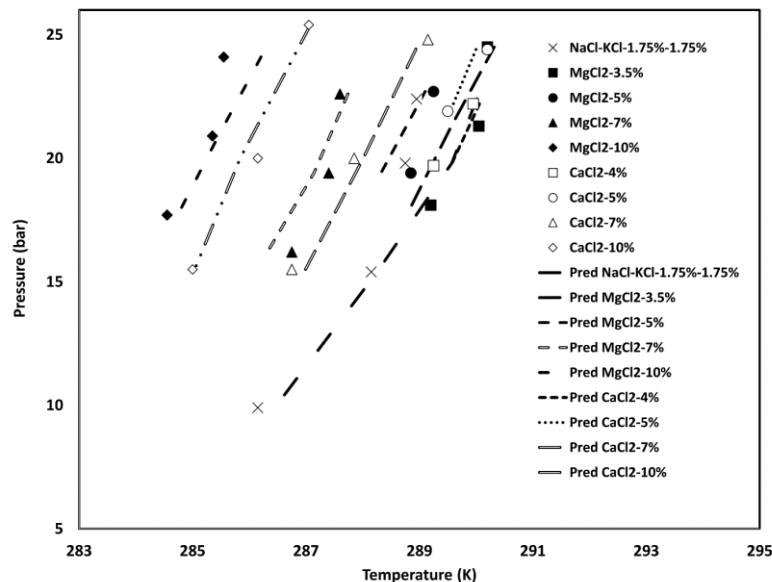


Fig. 1. Measured and predicted (vdW-P approach) equilibrium data of binary CP/CO₂ hydrate in pure water and brine.

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Macroscopic Insight into the Hydrate Decomposition Kinetics below Freezing Point of Water

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Depressurization is a promising technique for extracting gas contained within natural gas hydrate sediment. Most researchers agree that the gas production behavior found in hydrate-bearing sediments is an interfacial decomposition process. A better understanding of the kinetics of hydrate decomposition below the freezing point of water is essential to the development and design of future natural gas production from hydrate reservoirs.

To investigate the effects of particle size, or surface-area-to-mass ratio, on the depressurization decomposition process, approximately spherical methane hydrate samples with 11 mm, 18 mm, and 22 mm nominal diameters were prepared to represent hydrate particles macroscopically. Experiments on hydrate decomposition by depressurization were then conducted and the gas production percentage and production rate were measured. The results show that the effect of pressure is significant on the production percentage compared with that of the surface-area-to-mass ratio. With regards to production rates during decomposition, the extent of influence of production pressure is consistent with the surface-area-to-mass ratio. Cryogenic scanning electron microscopy (SEM) images of hydrate samples suggest that a hydrate larger in diameter has a smoother surface, which in turn could make it difficult for the ice cluster to attach to the hydrate surface. Ice clusters initially formed on the hydrate surface move, so a randomly distributed ice-layer shielding mechanism with different surface-area-to-mass ratios is proposed. Furthermore, no bound water was found to exist between pellets during production which could be deemed reliable for establishing the decomposition model.

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Formation and Growth of CO₂ and THF Hydrates in the presence of amino acid, amino acid derivatives and amino acid-based ionic liquids

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Gas hydrates (GHs) are ice-like solids that are stable at low temperatures and moderate pressures. GHs consist of gas molecules trapped within the hydrogen-bonded network of water. [1] While at one hand, the formation of GHs in pipelines is a nuisance for the oil/gas industry due to the blockage of the pipelines that results in huge production loss. Whereas, on the other hand, due to their ability to trap a large amount of gas in small volumes, GHs are becoming a potential source for carbon capture and sequestration (CCS) technology. [2]

The formation of hydrates is like a crystallization process that can be controlled by using chemical additives and physical methods as per the requirement. Generally, the hydrate additives are toxic compounds or are needed in large quantities. Thereby, greener, biocompatible, and low dosage additives are always in demand. [3]

In this work, we have studied the effect of several additives viz., amino acids (AAs), their derivatives (AADs), and ionic liquids based on amino acids (AAILs) on CO₂ (sl) and THF (sII) hydrates formation and growth through extensive thermodynamic and kinetic screening using a rocking cell apparatus. The phase behaviour of CO₂ hydrates in the presence of 10 wt% additives was studied. The AAILs shifted the equilibrium conditions towards lower temperatures and high pressures thereby showing thermodynamic inhibition capacity. A constant ramping methodology was used to obtain the hydrate onset nucleation temperatures in presence of 1 wt% additives. Most of the tested ILs were found to shift the onset nucleation temperatures towards higher subcooling, thereby acting as kinetic inhibitors. However, the trends were found to be pressure dependent. Isochoric-isothermal experiments were used to obtain the induction time at 1 °C in presence of additives. The isothermal measurements revealed that at lower concentrations many of the additives were acting as promoters for the CO₂ hydrates formation and growth.

The ILs were also tested for their effect on the THF (sII) hydrates formation and growth at atmospheric pressure. The results agreed well with the high-pressure measurements using the rocking cell apparatus. The morphology of the THF hydrates crystals was also recorded and it was found that the ILs do not alter the hydrate growth by adsorption at the crystal surface. These results reveal the potential of tested ILs as multi-purpose hydrate additives.

ACKNOWLEDGEMENT

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Effect of Host Framework on The Phase Behaviour and Nucleation of CO₂ Hydrates : Isotopic Effects

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Gas hydrates (GHs) are crystalline inclusion compounds where small gas molecules (guests) are accommodated within the three-dimensional hydrogen bond network of water (host). GHs are generally stable at low temperatures and moderately high pressures. Different size of guest gas molecules forms different hydrate structures [1]. The effect of additives on hydrate phase behaviour and formation is well documented but studies concerning the effect of different hosts are scarce [2].

In this work, we have studied the CO₂ hydrate phase equilibria and nucleation phenomena using H₂O, D₂O and their binary mixtures as hosts. It was found that the phase equilibrium shifts +2.3 K in H₂O compared to D₂O indicating a significant effect of isotopic substitution. Clausius-Clapeyron equation was used to obtain dissociation enthalpies at equilibrium conditions and found to be unchanged with the water fraction composition, which indicates no change in the hydrate cage structures. Similarly, a constant cooling method was used to obtain the onset nucleation temperature at an initial pressure of 3.5 MPa which indicates that nucleation always occurs between the melting temperature and the temperature of the maximum density (TMD) of the corresponding system. These measurements also indicate the metastable zone width of the studied systems. The results reported in this work indicates the magnitude of the isotopic effect on CO₂ hydrates formation and dissociation, which may have implications towards the application of hydrate technology for separation and purification processes.

Acknowledgement

Fundação para a Ciência e Tecnologia, FCT/MCTES (Portugal) for financial support through project PTDC/EQU-EQU/32050/2017. The work was partially supported by the Associate Laboratory for Green Chemistry - LAQV which is financed by national funds from FCT/MCTES (UIDB/50006/2020 and UIDP/50006/2020, and LA/P/0008/2020).

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Comparison of different viscosity models for two-phase liquids on the example of the oil-based ice slurry

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Gas hydrates are a challenge during the operation of industrial pipelines in terms of deposits and the formation of blockages. Finding ways to minimize the risk of blocking requires studying the properties of slurries laden by cohesive particles, particularly its rheology. Since it is not always possible to measure the viscosity of a two-phase fluid, various models can be applied to calculate it [1]. Some of them are simple and do not consider the flow structure and morphology of the particles. Others are more complex and require such data. The choice of the model is always tricky since the former may give irrelevant values, and the latter may be unavailable for use due to the lack of all necessary input data.

The aim of the work is to compare the relative viscosity of a cohesive slurry with ice particles (up to 20.3% vol.) determined by a semi-experimental method and by different models (Thomas [2], Brinkman [3], Mills [4], Bingham [5]). Decane is used as a carrier fluid. In the experiments, the relative viscosity was determined from the pressure drop across the flow loop in the slurry flow in a turbulent regime. The measured pressure drop was compared with the value obtained in the calculation procedure, taking into account the hydraulic resistances of the loop. The calculated pressure drop was brought into the best agreement with the measured values in the entire range of considered flow rates by varying the viscosity of the slurry in the calculation. As a result of the work, it was found that the pressure drop alters differently when the particle concentration increases. So, the drop at 400 kg/h was 0.124 bar for pure decane and 0.179 bar for 20.3% slurry (44.4% higher). At 2000 kg/h, the pressure drop was 1.09 bar vs. 1.147 bar (5.2% higher) for pure decane and 20.3% slurry, respectively. The relative viscosity of slurry also increases with increasing particle concentration (up to 4.3 times at 20.3%). The most rapid increase was observed at concentrations above 12%. The consideration of slurry as a Bingham fluid gave the best agreement among the other models. Up to a concentration of 12%, the Bingham model gives a relative viscosity comparable to other models. However, above 12%, the slurry's relative viscosity, according to the Bingham model, also increases rapidly, leading to better reproduction of semi-experimental data. As a result, an average discrepancy of 20.1% was obtained, while the error reached 58% for the other models.

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Paired KHI-MEG for synergistic inhibition of methane hydrate reformation

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The efficient and safe development of natural gas hydrate (NGH) resources is of great significance for ensuring and optimizing the utilization of energy in the future. Mitigating and controlling the regeneration of hydrate in the pipeline system is one of the challenges in the exploitation of NGH. In order to overcome the disadvantage of large injection amount of thermodynamic inhibitors (THIs) such as ethylene glycol (MEG), it is necessary to design a good synergistic inhibition strategy to improve cost efficiency and flow assurance. In recent years, more and more studies have reported the synergistic effect of THIs and kinetic inhibitors (KHIs). The synergistic inhibition of ethylene glycol (MEG) and kinetic inhibitor (KHI) PEO-co-VCap-1 on methane hydrate regeneration in the presence of fine sand was studied in a 500ml high-pressure reactor with pure methane gas. The concentration range of MEG and PEO-co-VCap-1 was controlled to be 0-5wt% and 0-0.5wt%. Four inhibitor formulations with different doses were carried out, and 12 groups of experiments were carried out. The results show that PEO-co-VCap-1 alone can delay the nucleation stage of hydrate, but it may lead to the disastrous growth of hydrate in a short time. Its combination with MEG can delay hydrate nucleation, effectively reduce the occurrence of catastrophic growth and reduce the risk of pipe blockage in oil and gas pipeline transportation. When the concentration of MEG was 5% and the concentration of PEO-co-VCap-1 was 0.5%, the synergistic inhibitory effect was very obvious, which could prolong the induction period of methane hydrate to more than 2800 min. The synergistic inhibitory effect of MEG and PEO-co-VCap-1 was similar to that of increasing temperature. This finding shows that if PEO-co-VCap-1 is used together with good synergists such as MEG, it will help kinetic inhibitors to be used in higher undercooling environment, and provide new possibilities for efficiently solving the problem of hydrate prevention and control in oil and gas production under high undercooling conditions.

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Discovering Hidden Structures of Clathrate Hydrates

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Clathrate hydrate has diverse crystal structures, among them, the three most prevalent ones covered nearly almost all hydrates, other structures are taken into account only when specific guest molecules are present. Here we report the observation of a hidden clathrate structure - the tetragonal structure (TS-I) in commonly formed gas hydrates, as evidenced from molecular dynamics simulations. We show that in a system supporting the formation of sI crystals, when two (or more) sI crystal grains with different growth directions come into contact or when the growth of sI crystal encounters geometrical frustration, the TS-I results as a co-crystal. And we give evidence that the TS-I may also play an important role in the combination and/or transition between sI and sII. These results hint that this previously neglected structure may be commonly present whenever sI and/or sII are formed. In a broader context, we suggest that confining the possible structures for common gas hydrates within three dominant structures may hinder an in-depth understanding of clathrate hydrates.

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A Critical Assessment of Gas Hydrates Phase Equilibria Predictions for Inhibited Systems with Salts and Organic Inhibitors

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Gas hydrates phase equilibria predictions for inhibited systems with salts and organic inhibitors are critical in a number of applications, with particular importance in the oil and gas as the prevention of hydrates is paramount for safe and continuous production. While there exists numerous methods and model for hydrate phase equilibria and inhibited systems, they all rely on fitting of specific data that rely on experimental measurements and are system specific by adjusting the water activity contribution to the chemical potential of water. We have shown that recently that a better approach is to treat gas hydrate inhibition as a colligative property, which causes the formation temperature, at a given pressure, of hydrates to be depressed with the presence of inhibitors (salts and organics), which remain in solution and are not part of the hydrate structure. This is directly analogous to the freezing point depression of water. This simple approach is fundamentally sound and accurate in capture all the available measured data in the literature, which demonstrates that reliable predictions can be made by simply knowing the change in the water activity in the presence of the inhibitors. The correlations developed for the water activity are universal and can be used for any range of concentration and combination of inhibitors. This approach is simple and reliable, and more broadly nearly represents the end of hydrate phase equilibria for inhibited systems. In the second part of this contribution, we will discuss the how different commonly used models/tools perform in the prediction of hydrate phase equilibria for inhibited systems, highlights their strengths and deficiencies.

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Functionalized Nanoparticles as Recyclable Hydrate Slurry Dispersants

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The agglomeration of the gas hydrate in the flowline may disrupt the normal operation and even block the pipeline to cause enormous financial loss. One of the current solutions is to inject one type of low-dosage hydrate inhibitors, anti-agglomerant, to prevent the agglomeration. The concerns using such chemicals are mainly about the cost, toxicity, and environment impact. More recently, nanoparticles are investigated to be a potential candidate that can disperse small hydrate particles and allow them to flow in a slurry form, for the benefit that can be more environmentally friendly and recyclable. In our work, we coated 23.5 nm iron oxide particles with different hydrophobicity and studied their performance to disperse small hydrate particles. The response of iron oxide nanoparticles to the magnetic field was utilized for the recycling compared to particles of other materials. Both in microscopic scale with in-situ observations at atmosphere and in macroscopic scale with rock-flow cell experiments. With proper surface modifications, the iron oxide nanoparticles prevented small hydrate particles from agglomeration. Further, we investigated recycling the particles with magnetic field efficiently after the test. By adding a very small amount of surfactant (0.5% to the water phase), the nanoparticles were fully detached from the oil-water interface, after drying, they were ready be reused, this can greatly save the cost and minimize the environmental concerns.

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Experimental Observations of Hydrate Deposition for Hydrate Management in Gas Filled Wellhead

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Hydrate formation near the wellhead is of particular concern due to the possible plugging of the well tubing line, resulting in significant operational loss in addition of creating potentially hazardous conditions. Especially, the shut-in and the eventual restart of a well represent the most concerning operation due to the favorable conditions for hydrate blockages. In a shut-in of a well, the top of the well up to the wellhead is gas-filled, and depending on the duration of the shut-in, the wellhead can be quickly cooled to ambient conditions, favoring the condensation of water at the top of the well or the pipe wall, which can lead to hydrate formation. This study investigates dependence of hydrate growth on the reservoir temperature to understand the behaviors of hydrate formation and deposition in a wellhead and to quantify the growth rate of hydrate deposition. It is found that insufficient convection and water condensation can delay hydrate deposition, with delayed growth, observed for the lower reservoir temperatures. Conversely, conditions inducing effective convection in the pipe and water condensation cause rapid growth of hydrate deposition with spike-like morphology. In order to understand the relationship between convection and water condensation, the fugacity of water at the wall and center of each section of each pipe section was compared. Water condensation started when the ratios of water fugacity at the wall and the center ($f_{w,wall}/f_{w,center}$) lower than 1.0, which indicates the vapor at the wall temperature is oversaturated, and hydrate wall deposition starts with the water condensation in the hydrate stable region. Significant hydrate formation was observed for $f_{w,wall}/f_{w,center} < 0.5$. Overall, this study provides further understanding and data for hydrate deposition by considering the reservoir temperature. Also, the results have insight into better management strategies for hydrate formation near the wellhead.

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Role of gas hydrate in the thermo-chemical evolution of Enceladus and Europa and potential detection by future space missions

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Space exploration of Jupiter and Saturn by the Galileo and Cassini-Huygens mission, respectively, has revealed that several icy bodies harbor liquid water underneath their cold icy surface, where large quantities of gas compounds may be stored in the form of clathrate hydrate (Tobie et al. 2012, Choukroun et al. 2013). Gas hydrates are expected to play a crucial role in the chemical evolution of these ocean worlds and their present-day activity. The detection of CO₂ and CH₄ in the watery jet emanating from its active south pole of Saturn's moon Enceladus (Watie et al. 2009, 2017) suggests that these two compounds may be in the form of gas hydrate in the hydrosphere of Enceladus and be partly decomposed during the eruption process. The IR spectral signatures of CO₂ clathrate (Oancea et al. 2012) have been identified at the vicinity of the jet sources, confirming the potential role of CO₂ clathrate hydrate (Combe et al. 2018, Robidel et al. 2020). This constitutes the first detection of gas hydrate outside the Earth. Vapor eruption have been also detected on Jupiter's moon Europa (Roth et al. 2014), suggesting again the potential role of gas hydrate. In this presentation, we will evaluate the conditions under which gas hydrate may form inside Enceladus and Europe, the efficiency of their transport from the seafloor to the icy surface, and how they may influence the eruptive activity. Using IR reflectance spectra acquired in the laboratory (Oancea et al. 2012, Nna Mvondo et al. 2020), we will discuss how CO₂ and CH₄ hydrates may be identified on Europa by ESA JUICE and NASA Europa Clipper, providing crucial information on on-going eruption activity.

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A critical review of testing techniques for evaluating the performance of Kinetic Hydrate Inhibitors

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Kinetic Hydrate Inhibitors (KHI) are regarded as Low Dosage Hydrate Inhibitors (LDHI), as their dose rates are normally less than 3% of the aqueous phase. They are becoming popular, in particular in offshore developments as they could significantly reduce footprint and weight requirement for hydrate inhibition facilities. KHIs could reduce the amount of MEG considerably, affecting CAPEX. They can be recovered from produced water, hence reducing OPEX and minimizing the effect on the environment.

Recent developments in testing techniques, i.e., Crystal Growth Inhibition (CGI) are becoming popular among experimentalists. However, some labs/companies find the procedure complicated and time-consuming, hence expensive. Therefore, some of the labs are still using the old Induction Time (IT) techniques. There are doubts on the results of the induction time technique, despite repeating the test 3-5 times. Definitely, running the induction time technique 3-5 times will make it more expensive/time-consuming than CGI method.

In this communication, we propose a modified Induction Time, called Induction Time Plus (IT⁺) that is repeatable/reliable. The technique is based on conducting the IT technique with a very small amount of hydrates (or hydrate memory). This technique removes the effect of nucleation on hydrate formation, as nucleation depends on many factors. In the technique the system is cooled-down to form hydrates, then the system is heated to around 1 °C above hydrate dissociation temperature, finally, the system is cooled down to the target temperature (at desired pressure) and monitored.

In this communication, the IT⁺ technique is described in detail with some examples. A critical review of testing techniques is presented at the end, summarizing the advantages and disadvantages of the three techniques.

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A Novel Method for the Determination of the Hydrate Induction Time through Temperature Steps

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Clathrate hydrates are supramolecular compounds formed when small (usually gaseous) molecules, such as methane, carbon dioxide, and hydrogen, interact with water under defined pressure and temperature conditions [1]. Natural gas hydrate formation causes plugs in oil and gas pipelines, representing a major problem in the gas and oil industry. Solutions adopted to manage hydrate-related problems are based on a lowering of the freezing point with the use of chemicals (Thermodynamic Inhibitors, TIs), or on interfering with hydrates growth by employing polymers or small molecules (Low-dosage Hydrate Inhibitors, LDHIs) [2,3]. The latter category may be divided into kinetic inhibitors (KHIs) and antiagglomerants (AAs) [4].

The evaluation of the induction times (IT), together with other measurements, is taken as an indication for the efficiency of hydrate inhibitors, and they are usually carried out by simply putting the experimental system under chosen P/T conditions and then waiting for the hydrate to form and measuring the time elapsed. However, it is a widely recognized problem that the time and temperature parameters measured are heavily dependent on a number of experimental parameters, thus hindering the comparison among different experimental setups [5]. Another well-known problem is that, particularly for IT measurements, the variance within a single experimental setup is intrinsically high, thus leading to define hydrate nucleation as a "stochastic" phenomenon [6].

Here we describe an improved procedure that can remarkably reduce the variability of measurements of hydrate induction times, while keeping a good correlation of measured values with the respective temperatures as obtained by a constant cooling method [7]. In this procedure, temperatures are lowered by 0.5 °C after each time span of 3 h with no hydrate formation. This "step induction time" (SIT) method gives less variable results in terms of measured ITs of several low-molecular weight hydrate inhibitors and promoters, and showed a higher correlation with inhibitor performances as determined by constant cooling as a usual IT method.

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Experimental and Computational Investigation of Newly Synthesized Ionic Liquid and Ionic Cellulose as Potential CH₄ Hydrate Inhibitors

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Gas hydrates have been considered as a nuisance in gas and oil industry, because hydrate formation in the transmission pipelines gives rise to serious economic and environmental damages. To prevent this problem, several types of hydrate inhibitors such as methanol, NaCl, and PVCap have been used. In particular, ionic liquids attracted increasing attention as gas hydrate inhibitors due to their unique function as both a thermodynamic hydrate inhibitor (THI) and a kinetic hydrate inhibitor (KHI). In this study, a new kind of ionic liquid, [DMIM][MP] (1,3-dimethylimidazolium methylphosphite), was synthesized and combined with cellulose, one of the most abundant organic compounds on Earth. Combining cellulose with the ionic liquid can contribute to lowering the hydrophobicity of cellulose and thus, improving its hydrate inhibition capability.

In this study, [DMIM][MP], cellulose, and ionic cellulose were appraised as potential KHIs for CH₄ hydrate using both experimental and computational methods. Their inhibition performance was compared with that of PVCap, one of the well-known commercial KHIs. The onset temperatures of CH₄ hydrate in the presence of potential inhibitors were measured using a high-pressure autoclave reactor. The onset temperature of CH₄ hydrate with [DMIM][MP] was the lowest and comparable to that with PVCap, indicating that [DMIM][MP] is the better KHI than other additives. The inhibition performance of ionic cellulose that was surface-modified with [DMIM][MP] was better than that of cellulose. Molecular dynamics simulations revealed that initial cage formation mechanisms did not differ depending on the types of inhibitors. However, 'cage adsorption' capability of each inhibitor during hydrate growth was found to be a dominant factor in determining their inhibition performance on CH₄ hydrate. The overall experimental and computation results provide deep insights into molecular inhibition mechanism of ionic liquids, cellulose, and ionic cellulose.

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Impact of salt (NaCl) concentration on water recovery with CO₂ hydrates evidenced by in-situ Raman Spectroscopy

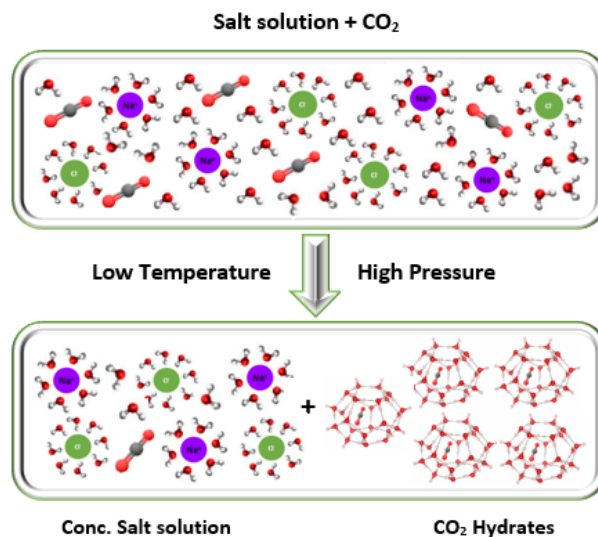
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The shortage of potable water and the release of greenhouse gases are both major challenges that will sternly exacerbate in future years and that need to be addressed as soon as possible. According to World Health Organization and UNICEF, 1 in 3 people globally do not have access to safe drinking water (WHO/UNICEF,2019), which could be attenuated with seawater desalination¹. Gas hydrate technology is one of the promising approaches to mitigate both ongoing challenges simultaneous CO₂ capture and water desalination². The process is depicted in the diagram below.

A unique in-situ Raman-coupled high-pressure stage is used to investigate the influence of salt (NaCl) concentration on water recovery with CO₂ hydrates. Raman spectroscopy is shown to be a sensitive tool to measure any disruption in the hydrogen bonded water network of the solution by probing OH-stretching vibrations. It is applied for the first time as a stand-alone technique to determine water recovery using the signature of water and corresponding calibration curves. CO₂ clathrates are synthesized from 15 and 3.5 wt.% salt solutions at temperatures below 0°C and pressure of ~2.5 MPa.

Analysis of the Raman molecular spectra of water demonstrates that the salt is primarily rejected from the forming CO₂ clathrate structure and contributes thereby to rise the saline water concentration around hydrate crystals. A decrease of salinity observed around the hydrates upon temperature increase is assigned to the progressive release of water molecules from the dissociating CO₂ clathrates. The impact of the initial salt content is further examined by in-situ Raman spectroscopy to identify the main factors that could enhance the water recovery process.



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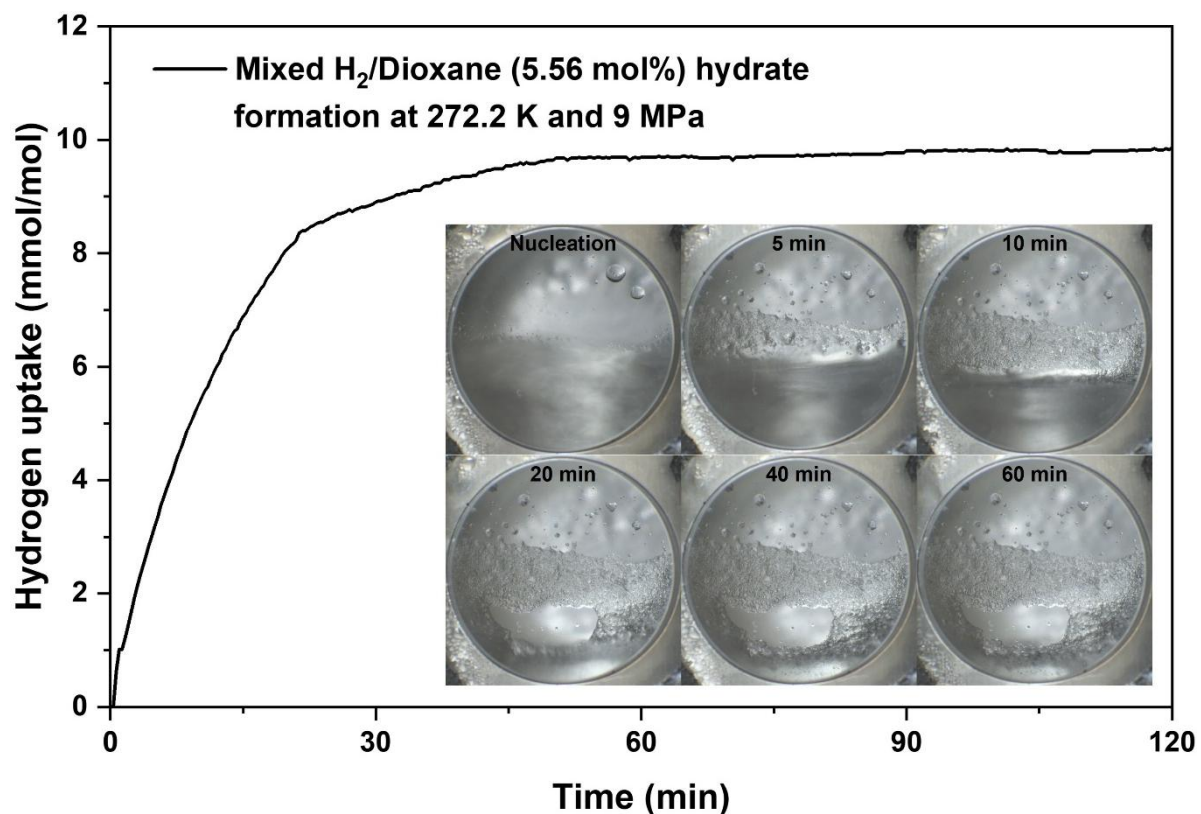
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A thermodynamic and kinetic study on the mixed H₂/Dioxane sII hydrate for hydrogen storage

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Hydrogen (H₂) as a renewable energy carrier with zero-emission upon combustion is projected to play an indispensable role in the future clean energy domain. Solidified hydrogen storage (Solid-HyStore) via clathrate hydrates that enables safe, long-term, and energy-dense storage of hydrogen molecules under moderate temperature and pressure conditions has immense potential for stationary hydrogen storage applications in the foreseeable hydrogen economy. Herein, 1,3-dioxane (Dioxane) was employed to moderate the temperature and pressure condition associated with the formation of H₂-containing clathrate hydrate. With the presence of stoichiometric Dioxane in the hydrate forming solution, an excellent consistency was observed among the phase equilibrium data of mixed H₂/Dioxane (5.56 mol%) hydrate obtained using the isochoric pressure search method and the dissociation along the phase boundary (PB) method, respectively. The mixed H₂/Dioxane (5.56 mol%) hydrate formation kinetics was studied comprehensively at various temperature and pressure conditions. Better hydrogen storage capacity was achieved at higher temperature and/or higher pressure while increasing temperature cut down the initial hydrogen uptake rate. The time-dependent optical images of three phase (hydrate, liquid, and gas) mixtures were acquired to illustrate the macroscopic hydrate growth behavior. The present results contribute to the development of hydrate based hydrogen storage technology.



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Water content measurements in liquid Ethane in equilibrium with water or hydrates: new measurements and literature data evaluation

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Abstract

A New Method, developed at Heriot-Watt Hydrate Research Centre, was used to determine water content measurements in rich liquid ethane in equilibrium with water or hydrate phase. The phase behaviour of the system (ethane + water) was modelled using the simplified Cubic-Plus-Association (sCPA) and Soave-Redlich-Kwong (SRK) equation of state combined with the van der Waals classical and non-density-dependent mixing rules, respectively. The targeted temperature range for the water content measurement is: -20 to 20 °C with pressures corresponding 242 Bar. To enhance understanding in terms of the repeatability and accuracy of the measurements presented, 120 water content measurements for liquid ethane in equilibrium with water were made. The sCPA model used only one adjustable parameter in contrast with the SRK model, which used three adjustable parameters. In all cases, the hydrate-forming conditions are modelled using the van der Waals and Platteeuw's solid solution theory. Additionally, the sCPA model predictions were compared against hydrate dissociation conditions from open literature.

Keywords: water content, liquid phase ethane, hydrate

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FROM CLATHRATE TO CLATHRITE IN OTHER OCEAN WORLDS

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Introduction: Clathrate hydrates are minerals potentially interesting for astrobiology that might have far-reaching implications on a planetary scale. Firstly, in the ice petrology field, clathrate hydrates formation and dissociation might promote the occurrence of endogenous processes such as cryovolcanism in Titan and Europa [1, 2] and gas emanations as Enceladus' plumes [3]. Secondly, temperature-pressure-salinity parameters of these ocean worlds might affect the stability and floatability of clathrates [3, 4], turning these clathrates into transport mechanisms for essential molecules for planetary habitability [5]. In this way, they might play a role in biogeochemical cycles of ocean worlds by trapping or releasing molecules after their dissociation. Furthermore, they might be behind stratification of Titanian alkanofers [6]. Besides, on Earth clathrate hydrate deposits are in themselves a microhabitat for bacterial communities focused on degrading hydrocarbons that the clathrate structure encapsulates [7]. As Earth is an inhabited planet, the past presence of these deposits (mainly CH₄ clathrate hydrates) are preserved in the geologic record as clathrites (aragonite/calcite/Mg-calcite), which might include evidences of bacterial mediation, if occurred during their formation [8, 9, 10]. The aim of this study is to synthesise and monitor the abiotic clathrite formation process from CO₂ clathrate hydrates under temperature-pressure conditions relevant to understand the European ice shell [11].

Methodology: Clathrite was synthesised inside a high-pressure simulation chamber made of stainless steel (volume capacity 67 ml). The high-pressure cell is connected to a tank of CO₂ (gas). It is complemented by thermocouple and pressure sensor to monitor both parameters and it is coupled Raman spectrometer so as to analyse phase changes. The chamber was filled with crushed ice formed by 7.4 wt% Ca(OH)₂ dissolution previously frozen. Once the chamber was pressurized at 30 bar, temperature was reduced down to 258 K to promote CO₂ clathrate formation. Subsequently, the chamber was heated slowly up to 248 K. Raman spectroscopy measurements using a 532 nm laser were taken to study the synthesis process of clathrite while pressure and temperature change. The mineralogy of final product of clathrite was also verified with X-ray diffraction technique.

Results: From the injection of CO₂ into chamber to the final stage of heating we observed carbonate precipitation. The final product phase obtained was calcite. Nevertheless, during experiment structure of carbonate in formation was modifying regarding clathrate stability, which was evidenced by the spectral signature within the ranges of 1078.24-1087.06 cm⁻¹ and 707.58-712.25 cm⁻¹ for stretching and bending vibration of the CO₃²⁻ ion respectively.

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Hydrate Deposition Characterization using Electrical Impedance Sensor in a Rock-Flow-Cell

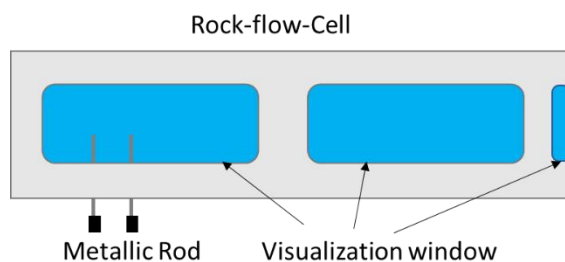
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Hydrate formation and blockage is one of the concerns in offshore oil and gas production. Early detection of hydrate deposition is critical for managing risks and to establish strategies to mitigate direct and indirect losses. In this context, sensing technologies are a key factor to enable a better understanding of the mechanism of hydrate formation and accumulation. In this work, electrical conductivity and permittivity techniques were used to evaluate hydrate formation and accumulation in a high-pressure rock-flow cell geometry. The rock-flow cell enables the measurement of other parameters as temperature, pressure and provides visual capabilities to compare the electrical impedance parameters with the phenomena and the other parameters.

The experiments were performed in a cylindrical rock-flow cell with an internal diameter of 51 mm and internal length of 500 mm. A metallic intrusive rod was used as a sensor to measure the electrical impedance. We installed cameras to an acquisition system so that we can synchronize the images with the electrical impedance sensors results.



For the hydrate formation we used the isochoric methodology. The system is composed by a liquid mixture of distilled water plus 0.1% NaCl, and synthetic gas (92 mol% methane + 8mol % propane). The initial pressure was 70 bar where hydrate equilibrium temperature for this pressure is 20°C.

The preliminary results indicate that we can detect the initial hydrate formation using the conductivity and permittivity parameters. The reference was the visual evaluation of small crystals. We can also relate the hydrate deposition thickness and water consumption with the sensor's measurements.

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Comparative study of the formation, the stability and the growth of methane hydrates in free, confined and ultra-confined organic environments by molecular modelling

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Gas hydrates are crystalline ice-like compounds composed of gas molecules (guest) which are trapped in polyhedral cells created within the hydrogen-bonded water framework (Sloan Jr, E.D.; Koh, C.; Clathrate hydrates of natural gases. CRC Press (2007). Gas hydrates have an ambiguous role by creating enormous problems for oil and gas industries but also by being considered as new materials for sustainable environment and energy storage. Therefore, it is important to better understand their formation, their stability, their growth and particularly at the microscopic level in order to determine the physical and chemical parameters which plays a key role.

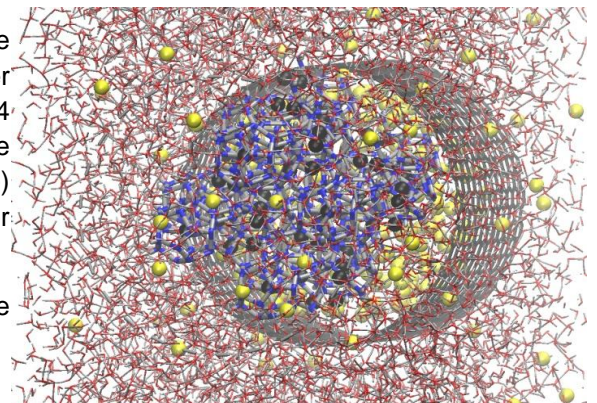
The presentation will focus in the first part on the stability of methane hydrates in the [2-273]K range by characterizing the structure and thermodynamical parameters in order to check the validity of the force field used for CH₄ as well as water.

Then we will focus on the growth and stability of methane hydrate in the absence/presence of a substrate (carbon nanotube (CN), graphene). In order to accelerate the formation, a methane hydrate nucleus is included within all systems and we study the influence of the substrate on the growth of this nucleus. Methodological developments are required to:

- identify potential methane molecules adsorbing onto the methane hydrate nucleus leading consequently to a rearrangement from liquid water molecules to polyhedral faces contributing then to the growth of the initial methane hydrate nucleus. This will enable us to determine the growth rate and compare it to experimental data.
- Convert the description of all species of the studied systems by coarse-grained force fields in order to accelerate the molecular dynamics calculations.

We will show the main differences of the methane hydrate growth at the interface of a CN full of methane in a water environment (see the figure on the right with yellow CH₄ escaping slowly the CN to diffuse and being adsorbed at the surface of the methane hydrate nucleus (black and blue) surrounded by water molecules (red) with a CN full of water in a methane environment.

We will also show the main differences between a methane hydrate adsorbed on a graphene surface or far from it.



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MHBS Geomechanical Studies: Maintaining Experimental Consistency

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ABSTRACT

There are large amounts of methane hydrate in soils under the permafrost of arctic regions and at the offshore within continental margins. The geomechanical study of methane hydrate-bearing soil (MHBS) is mainly in the context of ensuring the mechanical stability during gas extraction from MHBS reservoirs. The required mechanical parameters for geotechnical engineering are typically evaluated using geomechanical laboratories that are uniquely adapted to the environmental MHBS conditions. Because natural MHBS sampling for research purposes is a complex process, most of the laboratory investigations are conducted on artificial samples. MHBS artificial samples can be formed using different hydrates formation methods in the laboratory, where methane gas and water are supplied into the soil pore-space under the methane hydrate phase conditions. Limiting the gas or water amount during the formation process determines the hydrate saturation in the sample, which highly affects the MHBS mechanical behavior. As a result of a wide variety of testing facilities and experimental approaches that have developed in recent years, different measurement criteria and analyses have been suggested. The lack of uniformity among the various experimental investigations may adversely impact the reliability of integrating different test results for unified mechanical model development. This paper addresses fundamental aspects relevant to reliable MHBS geomechanical investigations, such as hydrate homogeneity in the sample, the hydrate formation duration criterion, the hydrate-saturation evaluation method, and the effect of temperature measurements accuracy. Finally, a set of recommendations for repeatable and reliable MHBS formation will be suggested, towards future standardization of MHBS geomechanical investigation.

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