



**ECGH 2024
EUROPEAN CONFERENCE
ON GAS HYDRATE**

**TRIESTE
ITALY**

ORGANIZATION



Umberta Tinivella - Michela Giustiniani - Giulia Alessandrini - Leonardo Riccucci



Rita Giovannetti - Marco Zannotti - Mirko Filippini



Leonardo del Rosso

Une école de l'IMT

Sophie Magand



Federico Rossi - Beatrice Castellani



Pietro Di Profio - Michele Ciulla - Serena Pilato

TRIESTE

CITY OF SCIENCE

Trieste boasts a long tradition as a dynamic hub for research, science and innovation, focused on sustainable growth and development, with an impact that extends beyond Italy to the rest of Europe and the developing world. It is internationally renowned for the high concentration of scientific institutions. The city hosts overall more than 30 national and international centers and companies working in research and higher education, 5000 permanent foreign scientists and some 13000 students and researchers.

Research Institutes, Universities, International Organizations and relevant scientific stakeholders founded the "Trieste City of Science" born in 2007 under the agreement of the "Protocol" aimed at:

- Disseminating scientific culture
- Supporting activities for the local economy based on knowledge and innovation
- Promoting Advanced Training
- Attracting Italian and foreign students and researchers
- Services for resident researchers and students
- Enhancing relations between research and business
- Organizing urban and territorial spaces
- Fostering social involvement through events, visits and other initiatives



ESOF2020
EUROSCIENCE OPEN FORUM
TRIESTE

 **OGS**

Moreover, Trieste has been nominated European City of Science 2020 under the initiative of the European Open Science Forum (ESOF). For the first time in its history, ESOF reached beyond the national borders of its host country. As a Central European city, Trieste was committed to strengthening the links with Central and Eastern European scientists, entrepreneurs, policy makers and citizens, thus making a crucial step towards a truly open and inclusive Europe. The city's natural spirit of openness and inclusiveness was expressed in the motto that Trieste had chosen for ESOF2020: "Freedom for science, science for freedom".

LOCATION



Auditorium SISSA (ICTP)

Via Beirut 2
34014 Trieste (TS)
Italia

Tel.+39 040 21401
Fax.+39 040 327307

PROGRAM ECGH2024 – Trieste 11-14 June 2024

Tuesday 11th - 14:00 - 18:00

14:00 - 14:15 **Open Ceremony**

14:15 - 14:45 **Keynote Lecture.**

Beyond Flow Assurance - Opportunities and Challenges with Gas Hydrates. **Peter Englezos**

14:45 - 16:45 **Session 1 – Chair Claire Pirim and Bohui Shi**

Mesomorphology of Clathrate Hydrates from Molecular Ordering. **Carlos L. Bassani,**
Understanding the Influence of Nano-Bubbles on CO₂ Hydrate Growth: An Investigation from Experimental and Molecular Dynamics Simulation. **Parisa Naeiji**

Investigation of the crystallization kinetics of pure and mixed hydrates from mixtures of carbon dioxide and methane. **Baptiste Bouillot**

Promoting effect of a natural peptide on methane-hydrate formation: insights from experiments and molecular-dynamics simulations. **Bastien Radola**

Molecular dynamics simulations of the effect of anti-agglomerant and wax molecular on methane hydrate growth. **Yumo Zhu. Candidate to the best oral presentation**

Investigating Deuterated Clathrate Hydrates as Novel Moderator Material for Very Cold Neutrons – A Neutron Scattering Study. **Valentin Czamler. Candidate to the best oral presentation**

The Impact of Alcohol and Ammonium Fluoride on Pressure-Induced Amorphization of Cubic Structure I Clathrate Hydrates. **Lilli-Ruth Fidler. Candidate to the best oral presentation**

Investigation of [BMIM]FeCl₄ ionic liquid as hydrate promotor for carbon capture from seawater. **Angsar Serikkali. Candidate to the best oral presentation**

16:45 - 17:15 **Coffee Break**

17:15 - 18:00 **Session 1 – Chair Marco Zannotti and Bohui Shi**

Effect of perchloric acid on the thermodynamics of tetrahydrofuran and mixed methane/tetrahydrofuran hydrates. **Dounya Frah. Candidate to the best oral presentation**

Emptied hydrates as advanced functional materials: from a scientific curiosity to hydrogen storage applications. **Leonardo del Rosso**

Experimental determination of stable and metastable equilibria involving CO₂ hydrate, ice, liquid water and gaseous CO₂. **Abdelhafid Touil**

19:00 **Icebreaker “Caffè degli Specchi”, Piazza Unità d'Italia, 7, Trieste center**

A transfer service is scheduled to depart from ICTP at 18:15 directly to the city center



Wednesday 12th - 9:15 - 18:00

9:15 - 10:30 **Session 2 - Chair Ana Cameirao**

Cases where it would be difficult to detect the causes of blockage. **Bahman Tohidi**
Experiments and Modeling of Gas Hydrate Wall Deposition Mechanisms in Multiphase Sheared Systems. **Rigoberto E. M. Morales**

Influence of hydrate-like particles in stratified and slug multiphase flow. **Vitor Machado.**
Experimental investigation of gas hydrate formation in crude oil and high salinity system. **Moises A. Marcelino Neto.**

A Transient Model to Predict Hydrate Slurry Flow in Horizontal Undulating-Pass in Gas/Oil/Water-Dominated systems. **Haoqi Chen. Candidate to the best oral presentation**

10:30 - 11:15 **Coffee break and Poster sessions**

11:15 - 12:30 **Session 2 - Chair Rigoberto Morales**

Oil/Water Partitioning of Environmentally Improved Anti-Agglomerant Low Dosage Hydrate Inhibitor. **Regan Jones**

Sustainability Benefits of Switching from Thermodynamic Hydrate Inhibitors to Anti-Agglomerant Low Dosage Hydrate Inhibitors. **Jeremy Bartels**

Gas-Liquid Flow Experiments and Modeling in a Novel Rocking and Rolling Flow Loop. **Madina Naukanova. Candidate to the best oral presentation**

Transportability of a hydrate slurry in the presence of wax. **Lino Luiz Meneghel. Candidate to the best oral presentation**

Mechanistic Model of Hydrate Deposition Processes in Horizontal Oil-Dominated Flows. **Enqi Guo. Candidate to the best oral presentation**

12:30 – 12:45 **Groupement De Recherche (GDR) Hydrates de Gaz. Arnaud Desmedt**

12:45 - 14:00 **Lunch pack included, to be enjoyed in the outdoor areas of ICTP**

14:00 - 14:45 **Session 2 - Chair Michele Ciulla**

Efficient Gas Hydrate Characterization for Flow Assurance: A Focus on Thermodynamic and Kinetic Analysis. **Ernesto Petteruti**

Experimental determination of methane diffusivity in water and brine under hydrate formation conditions. **Thales Henrique Sirino.**

Study on the hydrate dissociation in the high-pressure flow loop. **Shangfei Song**

14:45 - 16:00 **Session 3 – Chair Jasmina Obhodaš**

Impact of Salts on CO₂ Hydrates and Injectivity during CO₂ Storage in Depleted Gas Fields. **Mahnaz Aghajanloo**

Water content measurements for pure CO₂ and a CO₂-rich mixture in equilibrium with hydrates at 253 to 283 K and 3000 to 6000 psia using the DSH analytical technique. **Larissa Torres. Candidate to the best oral presentation**

A novel high-pressure acoustic apparatus to investigate gas hydrate formation and distribution in porous media. Agnissan Art. **Clarie Constant. Candidate to the best oral presentation**

Exploring the Minimum Detectable Concentration of Methane Hydrate Using Associated Alpha Particle Technique. **Josip Batur. Candidate to the best oral presentation**

Kinetic Study of Binary Gas Mixtures for Understanding Mechanism of Hydrate Formation in the Sea of Marmara: Experimental and Molecular Dynamics Simulation Approaches.

Atousa Heidari. Candidate to the best oral presentation

16:00 - 16:45 **Coffee break and Poster Sessions**

16:45 - 18:00 **Session 3 – Chair Michela Giustiniani**

Unraveling the dynamics of gas hydrate formation and methane migration in the western Black Sea: Insights from a basin-scale numerical model. **Ewa Burwicz-Galerie**

Seafloor Pockmarks on the Chatham Rise, New Zealand – Could CO₂ Hydrate be Involved in Their Formation? **Ingo Pecher**

Exploring the efficiency of microbial anaerobic oxidation of methane as sink to hydrate-sourced methane. **Maria Ruiz De La Fuente**

Effects of Methane Hydrate Phase Transition on Deformable Sediment Structure Evolution under Cold Seep System. **Xuan Kou. Candidate to the best oral presentation**

Image-based pore network model to investigate hydrate pore habit effect on dynamic permeability evolution in hydrate-bearing sediments. **Mingqiang Chen. Candidate to the best oral presentation**

19:30 **Young and Science at Caffè' San Marco, via Battisti 18/A, Trieste center**

Thursday 13th - 9:00 - 12:30

9:00 - 10:30 **Session 4 – Chair Beatrice Castellani**

Energy and Economic Analysis on Different Technologies of Natural Gas Storage. **Ahmed Omran**

New Insights into the self-preservation phenomenon of methane hydrates. **Belkacem Samar. Candidate to the best oral presentation**

Hybrid Promoters for Synergistic Enhancement of Thermodynamic Stability of Methane Hydrates. **Seol Jiwoong**

Risk management for natural gas-hydrogen blend hydrate formation in pipeline transport. **Jeong-Hoon Sa**

A Novel Method for Natural Gas Hydrate Production: Depressurization and Backfilling with In-situ Supplemental Heat. **Yuxuan Li. Candidate to the best oral presentation**

Prospects for hydrate-based energy storage technologies. **Andrey Stoporev**

10:30 - 11:00 **Coffee break and Poster sessions**

11:00 - 12:45 **Session 4 – Chair Nick O'Neill**

Clathrate hydrates: A cool way to store carbon dioxide permanently. **Linga Praaven**

Evaluation Of 1,1-Difluoroethane as hydrate former for hydrate based produced water desalination. **Nagu Daraboina**

A Dual Hydrate-Based Desalination and CO₂ Capture Process: A Raman Spectroscopy Approach. **Bertrand Chazallon**

Rheological characterization of various mixtures of CO₂ hydrate slurries for low temperature refrigeration applications. **Rihab Khirallah. Candidate to the best oral presentation**

Phase equilibrium of CO₂ and Xe hydrate crystals in presence of food products. **Boumaiza Houaria. Candidate to the best oral presentation**

On the use of gas hydrates by a CO₂-based electrothermal energy storage system: modeling and evaluation. **Ioannis N. Tsimpanogiannis**

CO₂ hydrates crystallization kinetic parametric study: effect of impeller type. **Véronique Osswald. Candidate to the best oral presentation**

12:45 - 14:00 **Lunch pack included, to be enjoyed in the outdoor areas of ICTP.**

15:00 - 18:00 **Visit to the multidisciplinary Research Center ELETTRA Sincrotrone. A transfer service is scheduled to depart from ICTP at 2:30pm and return directly to the city center after the visit.**

19:30 **Social Dinner at Savoy Restaurant, Riva del Mandracchio, 4, Trieste Center**

Friday 14th - 9:30 - 14:00

9:30 - 11:00 **Session 4 – Chair Zhenyuan Yin**

Ultra-rapid CO₂ hydrate formation kinetics enabled by magnesium coupled with amino acid as promoter. **Yan Li. Candidate to the best oral presentation**

CCS - CO₂ hydrate formation kinetics in porous media under depleted reservoir storage conditions. **Peyman Dehghani. Candidate to the best oral presentation**

Pore-scale investigation of the effect of heterogeneous permeability on CO₂ hydrate kinetics. **Lifei Yan**

Sustainable CO₂ Capture in Seawater: Exploring L-Tryptophan Kinetic Promotion in Fresh and Saline Environments. **Abdelhafid Ait Blal**

Experimental and Computational Investigation on Multiphase Flow Behavior of CO₂ injection into Deep-Sea Sediment. **Yohan Lee**

Geological CO₂ storage in subsurface tested in microfluidics coupled with microscope and Raman spectroscopy. **Qian Ouyang. Candidate to the best oral presentation**

11:00 - 11:30 **Coffee break and Poster sessions**

11:30 - 12:30 **Session 4 – Chair Beatrice Castellani**

Hydrate-based gas separation of systems including hydrogen in porous media: A thermodynamic approach. **Saheb Maghsoodloo**

Optimizing H₂ uptake in H₂-THF hydrate and its mechanism: Implication on hydrate-based H₂ storage. **Zhenyuan Yin**

Improvement of hydrogen clathrate formation by reverse micelles and optimization of the formulative parameters. **Michele Ciulla**

Hydrogen storage in C₂ hydrogen hydrate. **Tomasz Poreba**

12:30 - 13:15 **Session 5 – Chair Leonardo del Rosso, Bertrand Chazallon and Elodie Gloesener**

Gas hydrates as indicators of cryomagmatic processes on Ocean worlds. **Victoria Muñoz-Iglesias**

Gas separation and storage in mixed clathrate hydrates as studied by molecular simulations: Applications to astrophysical contexts. **Antoine Patt**

Exploring the stability and new structures of gas filled ices up to Mbar pressures. **Livia Bove**

13:15 - 13:25 **Best poster and best oral presentation awards**

13:25 - 13:35 **Presentation of the 2026 ECGH-ICGH. Jean-Michel Herri**

13:35 - 14:00 **Presentation of the Candidatures to host the 2028 ECGH and goodbye to the next ECGH edition!**

14:00 **Lunch pack included, to be enjoyed in the outdoor areas of ICTP.**



Poster Session

Session 1

Thermodynamic criterion for predicting phase coexistence between two clathrate structures with different composition. **Vincent Ballenegger**

Unraveling the effect of double occupancy in N₂ gas hydrates. **Ludovic Martin-Gondre**
Relative thermodynamic stability of gas hydrate structures from Lattice-Switch Monte Carlo simulations. **Olivia Moro. Candidate to the best poster presentation**

Flue gas and desalination from seawater: thermodynamics and kinetic influence of salt and cooling rate. **Jean-Michel Herri**

CO₂ sequestration via gas hydrates: Raman and morphological characterization of CO₂, CH₄ and CO₂/CH₄ gas hydrates. **Marco Zannotti**

Session 2

Analysis parameters for evaluating gas hydrate kinetic inhibitor by pressurized microcalorimetry. **Fagner Cabral. Candidate to the best poster presentation**

Deposition and agglomeration characteristics of gas hydrates in natural gas pipelines by using chemical additives. **Seongah Park. Candidate to the best poster presentation**

Novel method and device to detect gas hydrates formation likelihood inside a pipeline. **Simone Arca**

Understanding Methane Hydrate Adhesion on Surfaces: A Preliminary Investigation. **Serena Pilato.**

Direct-Imaging System Using Electrical Impedance for Hydrates Monitoring in Rock-Flow Cell. **Jean P. N. Longo**

Session 3

Subsurface heat, salt and other inhibitors of methane hydrate stability in the Mediterranean Basin. **Angelo Camerlenghi**

Direct hydrate-based CO₂ sequestration in marine environments: lessons learned from CO₂-CH₄ replacement in natural gas hydrates. **Beatrice Castellani**

Dynamic of the gas hydrate/free gas system based on geophysical analysis and paleo-BSR modeling. **Umberta Tinivella**

Fabrication of silica gel-clathrate hydrate composite for improved CO₂ storage efficiency. **Siyoon Jeong. Candidate to the best poster presentation**

Geophysical evidence for gas hydrate/free gas associated with mud volcanism in the western Ross Sea (Antarctica). **Martina Busetti**

Reprocessing of 2D seismic data for the search of gas hydrates in the Eastern Mediterranean region. **Agnese Chies. Candidate to the best poster presentation**

Temporal variability of the stability field of methane hydrates in the oceans. **Leonardo Riccucci. Candidate to the best poster presentation**

Storage of methane and carbon dioxide in sediments. **Daria Sergeeva. Candidate to the best poster presentation**

Session 4

A novel experimental methodology for investigating the growth kinetics and porous structure of surfactant-promoted gas hydrate. **Daniel Broseta**

Understanding the influence of TRP on the kinetics of CO₂ hydrates growth using molecular dynamics simulation. **Xinrui Cai. Candidate to the best poster presentation**

Partition of CO₂ into clathrate hydrate cages: investigation by vibrational spectroscopy. **Rima Haidar. Candidate to the best poster presentation.**

Molecular simulations of mixed clathrate hydrates including ionic species. **Victoire Meko Fotso. Candidate to the best poster presentation**

Optimizing Biogas Upgrading with Clathrate Hydrates: Influence of Different Water Phases and Additives. **Rafal Damian Wolicki. Candidate to the best poster presentation**

Phase equilibria and formation kinetics of CF₃I hydrates as clean fire extinguishing agents. **Jonghwan Lee. Candidate to the best poster presentation**

Cation and anion effects of imidazolium based ionic liquids on Kinetic properties of methane hydrate formation in imidazolium based ionic liquids combined Cl⁻ and FeCl₄. **Suhyeon Son. Candidate to the best poster presentation**

Potential kinetic promoters for CO₂/CH₄ separation: IR vs in-situ Raman determinations. **Nadia Barbacane. Candidate to the best poster presentation**

Molecular insights into hybrid Methane physisorption-hydrate formation in spiral halloysite nanotubes: Implications for energy storage. **Fengyi Mi. Candidate to the best poster presentation**

Optimizing the formation of hydrates for highly efficient CO₂ capture. **Doyeon Kim. Candidate to the best poster presentation**

Towards storing and transporting gases in the hydrate form. **Matvei Semenov**

Session 5

Spectroscopic study of the methane hydrate at high pressure and temperature. **Selene Berni. Candidate to the best poster presentation**

Methane Outgassing from Clathrate Hydrates on Titan: Partial Dissociation and Substitution Mechanisms. **Elodie Gloesener**

Ammonia incorporation in methane clathrate within the subsurface ocean of Titan. **Shunsuke Nozaki. Candidate to the best poster presentation**

The conference secretariat will be open during the conference days from 9 am to 17 pm. For further information, please contact the organizing secretariat at the following contacts: ecgh2024@theoffice.it - +39 338 3387091

Table of contents

| | |
|---|----------|
| Session 1: Fundamentals | 1 |
| Thermodynamic criterion for predicting phase coexistence between two clathrate structures with different composition, Ballenegger Vincent [et al.] | 2 |
| Mesomorphology of Clathrate Hydrates from Molecular Ordering, Bassani Carlos [et al.] | 3 |
| Investigation of the crystallization kinetics of pure and mixed hydrates from mixtures of carbon dioxide and methane, Bouillot Baptiste [et al.] | 4 |
| Investigating Deuterated Clathrate Hydrates as Novel Moderator Material for Very Cold Neutrons – A Neutron Scattering Study, Czamler Valentin [et al.] . . . | 5 |
| Emptied hydrates as advanced functional materials: from a scientific curiosity to hydrogen storage applications, Del Rosso Leonardo [et al.] | 6 |
| Effect of perchloric acid on the thermodynamics of tetrahydrofuran and mixed methane/tetrahydrofuran hydrates, Frah Dounya [et al.] | 7 |
| The Impact of Alcohol and Ammonium Fluoride on Pressure-Induced Amorphization of Cubic Structure I Clathrate Hydrates, Fidler Lilli-Ruth [et al.] | 8 |
| Unraveling the effect of double occupancy in N ₂ gas hydrates, Martin-Gondre Ludovic | 9 |
| Relative thermodynamic stability of gas hydrate structures from Lattice-Switch Monte Carlo simulations, Moro Olivia [et al.] | 10 |
| Understanding the Influence of Nano-Bubbles on CO ₂ Hydrate Growth: An Investigation from Experimental and Molecular Dynamics Simulation, Naeiji Parisa [et al.] | 11 |

| | |
|---|-----------|
| Promoting effect of a natural peptide on methane-hydrate formation: insights from experiments and molecular-dynamics simulations, Radola Bastien [et al.] . . . | 12 |
| Flue gas and desalination from seawater : thermodynamics and kinetic influence of salt and cooling rate, Serikkali Angsar [et al.] | 13 |
| Investigation of (BMIM)FeCl ₄ ionic liquid as hydrate promotor for carbon capture from seawater, Serikkali Angsar [et al.] | 14 |
| Experimental determination of stable and metastable equilibria involving CO ₂ hydrate, ice, liquid water and gaseous CO ₂ , Touil Abdelhafid [et al.] | 15 |
| CO ₂ sequestration via gas hydrates: Raman and morphological characterization of CO ₂ , CH ₄ and CO ₂ /CH ₄ gas hydrates, Zannotti Marco | 16 |
| Molecular dynamics simulations of the effect of anti-agglomerant and wax molecular on methane hydrate growth, Zhu Yumo [et al.] | 17 |
| Session 2: Flow assurance and flow modeling | 18 |
| Novel method and device to detect gas hydrates formation likelihood inside a pipeline, Arca Simone [et al.] | 19 |
| Sustainability Benefits of Switching from Thermodynamic Hydrate Inhibitors to Anti-Agglomerant Low Dosage Hydrate Inhibitors, Bartels Jeremy [et al.] | 20 |
| Analysis parameters for evaluating gas hydrate kinetic inhibitor by pressurized microcalorimetry, Cabral Fagner [et al.] | 21 |
| A Transient Model to Predict Hydrate Slurry Flow in Horizontal Undulating-Pass in Gas/Oil/Water-Dominated systems, Chen Haoqi [et al.] | 22 |
| Experimental investigation of gas hydrate formation in crude oil and high salinity systems, De Vasconcelos Luiz Fernando Santos [et al.] | 23 |
| Mechanistic Model of Hydrate Deposition Processes in Horizontal Oil-Dominated Flows, Guo Enqi [et al.] | 24 |
| Oil/Water Partitioning of Environmentally Improved Anti-Agglomerant Low Dosage Hydrate Inhibitor, Jones Regan [et al.] | 25 |
| Study on the hydrate dissociation in the high-pressure flow loop, Liu Lihao [et al.] | 26 |
| Direct-Imaging System Using Electrical Impedance for Hydrates Monitoring in Rock-Flow Cell, Longo Jean P. N. [et al.] | 27 |

| | |
|--|-----------|
| Influence of hydrate-like particles in stratified and slug multiphase flow, Machado Vitor [et al.] | 28 |
| Transportability of a hydrate slurry in the presence of wax, Meneghel Lino Luiz [et al.] | 29 |
| Gas-Liquid Flow Experiments and Modeling in a Novel Rocking and Rolling Flow Loop, Naukanova Madina [et al.] | 30 |
| Deposition and agglomeration characteristics of gas hydrates in natural gas pipelines by using chemical additives, Park Seongah [et al.] | 31 |
| Efficient Gas Hydrate Characterization for Flow Assurance: A Focus on Thermodynamic and Kinetic Analysis, Petteruti Ernesto [et al.] | 32 |
| Understanding Methane Hydrate Adhesion on Surfaces: A Preliminary Investigation, Pilato Serena [et al.] | 33 |
| Experimental determination of methane diffusivity in water and brine under hydrate formation conditions, Sirino Thales Henrique [et al.] | 34 |
| Cases where it would be difficult to detect the causes of blockage, Tohidi Bahman | 35 |
| Session 3: Natural gas hydrate systems and climate change | 36 |
| Impact of Salts on CO ₂ Hydrates and Injectivity during CO ₂ Storage in Depleted Gas Fields, Aghajanloo Mahnaz [et al.] | 37 |
| A novel high-pressure acoustic apparatus to investigate gas hydrate formation and distribution in porous media, Agnissan Art-Clarie Constant [et al.] | 38 |
| Exploring the Minimum Detectable Concentration of Methane Hydrate Using Associated Alpha Particle Technique, Batur Josip [et al.] | 39 |
| Unraveling the dynamics of gas hydrate formation and methane migration in the western Black Sea: Insights from a basin-scale numerical model, Burwicz-Galerne Ewa [et al.] | 40 |
| Subsurface heat, salt and other inhibitors of methane hydrate stability in the Mediterranean Basin, Camerlenghi Angelo [et al.] | 41 |
| Direct hydrate-based CO ₂ sequestration in marine environments: lessons learned from CO ₂ -CH ₄ replacement in natural gas hydrates, Castellani Beatrice [et al.] . | 42 |

| | |
|---|-----------|
| Image-based pore network model to investigate hydrate pore habit effect on dynamic permeability evolution in hydrate-bearing sediments, Chen Mingqiang [et al.] | 43 |
| Reprocessing of 2D seismic data for the search of gas hydrates in the Eastern Mediterranean region, Chies Agnese [et al.] | 44 |
| Exploring the efficiency of microbial anaerobic oxidation of methane as sink to hydrate-sourced methane, De La Fuente Ruiz Maria [et al.] | 45 |
| Geophysical evidence for gas hydrate/free gas associated with mud volcanism in the western Ross Sea (Antarctica), Geletti Riccardo [et al.] | 46 |
| Kinetic Study of Binary Gas Mixtures for Understanding Mechanism of Hydrate Formation in the Sea of Marmara: Experimental and Molecular Dynamics Simulation Approaches, Heidari Atousa [et al.] | 47 |
| Fabrication of silica gel-clathrate hydrate composite for improved CO2 storage efficiency, Jeong Siyoon [et al.] | 48 |
| Effects of Methane Hydrate Phase Transition on Deformable Sediment Structure Evolution under Cold Seep System, Kou Xuan [et al.] | 49 |
| Seafloor Pockmarks on the Chatham Rise, New Zealand – Could CO2 Hydrate be Involved in Their Formation?, Pecher Ingo [et al.] | 50 |
| Temporal variability of the stability field of methane hydrates in the oceans, Riccucci Leonardo [et al.] | 51 |
| Storage of methane and carbon dioxide in sediments, Sergeeva Daria [et al.] | 52 |
| Dynamic of the gas hydrate/free gas system based on geophysical analysis and paleo-BSR modeling, Tinivella Umberta [et al.] | 53 |
| Water content measurements for pure CO2 and a CO2-rich mixture in equilibrium with hydrates at 253 to 283 K and 3000 to 6000 psia using the DSH analytical technique., Torres Larissa [et al.] | 54 |
| Session 4: Hydrate based and energy efficient technologies | 55 |
| Sustainable CO2 Capture in Seawater: Exploring L-Tryptophan Kinetic Promotion in Fresh and Saline Environments, Ait Blal Abdelhafid [et al.] | 56 |
| Phase equilibrium of CO2 and Xe hydrate crystals in presence of food products, Boumaiza Houaria | 57 |

| | |
|---|----|
| Evaluation of 1,1-Difluoroethane as hydrate former for hydrate based produced water desalination, Babu Ponnivalavan [et al.] | 58 |
| Potential Kinetic Promoters for CO ₂ /CH ₄ Separation: IR vs in-situ Raman determinations, Barbacane Nadia [et al.] | 59 |
| Understanding the influence of TRP on the kinetics of CO ₂ hydrates growth using molecular dynamics simulation, Cai Xinrui [et al.] | 60 |
| Improvement of hydrogen clathrate formation by reverse micelles and optimization of the formulative parameters, Ciulla Michele [et al.] | 61 |
| CCS - CO ₂ hydrate formation kinetics in porous media under depleted reservoir storage conditions., Dehghani Peyman [et al.] | 62 |
| Partition of CO ₂ into clathrate hydrate cages: investigation by vibrational spectroscopy, Haidar Rima [et al.] | 63 |
| Rheological characterization of various mixtures of CO ₂ hydrate slurries for low temperature refrigeration applications, Khirallah Rihab [et al.] | 64 |
| Optimizing the formation of hydrates for highly efficient CO ₂ capture, Kim Doyeon [et al.] | 65 |
| On the use of Gas Hydrates by a CO ₂ -based Electrothermal Energy Storage System: Modeling and Evaluation, Kyriakides A.-S. [et al.] | 66 |
| Phase equilibria and formation kinetics of CF ₃ I hydrates as clean fire extinguishing agents, Lee Jonghwan [et al.] | 67 |
| Experimental and Computational Investigation on Multiphase Flow Behavior of CO ₂ injection into Deep-Sea Sediment, Lee Yohan [et al.] | 68 |
| Ultra-rapid CO ₂ hydrate formation kinetics enabled by magnesium coupled with amino acid as promoter, Li Yan [et al.] | 69 |
| A Novel Method for Natural Gas Hydrate Production: Depressurization and Backfilling with In-situ Supplemental Heat, Li Yuxuan [et al.] | 70 |
| Clathrate hydrates: A cool way to store carbon dioxide permanently., Linga Praveen | 71 |
| Molecular simulations of mixed clathrate hydrates including ionic species, Meko Fotso Victoire [et al.] | 72 |
| Hydrate-based gas separation of systems including hydrogen in porous media: A thermodynamic approach, Maghsoodloo Saheb [et al.] | 73 |

| | |
|--|----|
| Molecular insights into hybrid Methane physisorption-hydrate formation in spiral halloysite nanotubes: Implications for energy storage, Mi Fengyi [et al.] | 74 |
| Geological CO ₂ storage in subsurface tested in microfluidics coupled with microscope and Raman spectroscopy, Ouyang Qian [et al.] | 75 |
| Energy and Economic Analysis on Different Technologies of Natural Gas Storage, Omran Ahmed [et al.] | 76 |
| CO ₂ hydrates crystallization kinetic parametric study: effect of impeller type, Oswald Véronique [et al.] | 77 |
| Hydrogen storage in C ₂ hydrogen hydrate, Poreba Tomasz [et al.] | 78 |
| A novel Experimental Methodology For Investigating The Growth Kinetics And Porous Structure Of Surfactant-Promoted Gas Hydrate, Samar Belkacem [et al.] | 79 |
| New Insights into the self-preservation phenomenon of methane hydrates, Samar Belkacem [et al.] | 80 |
| Risk management for natural gas-hydrogen blend hydrate formation in pipeline transport, Sa Jeong-Hoon [et al.] | 81 |
| Towards storing and transporting gases in the hydrate form, Semenov Matvei [et al.] | 82 |
| Hybrid Promoters for Synergistic Enhancement of Thermodynamic Stability of Methane Hydrates, Seol Jiwoong | 83 |
| HyPurTex: Elevating Textile Wastewater Purification for Sustainable Production, Sharma Subhash [et al.] | 84 |
| Cation and anion effects of imidazolium based ionic liquids on Kinetic properties of methane hydrate formation in imidazolium based ionic liquids combined Cl ⁻ and FeCl ₄ ⁻ , Son Suhyeon [et al.] | 85 |
| Prospects for hydrate-based energy storage technologies, Stoporev Andrey [et al.] | 86 |
| Optimizing Biogas Upgrading with Clathrate Hydrates: Influence of Different Water Phases and Additives, Wolicki Rafal Damian [et al.] | 87 |
| Pore-scale investigation of the effect of heterogeneous permeability on CO ₂ hydrate kinetics, Yan Lifei [et al.] | 88 |
| Optimizing H ₂ uptake in H ₂ -THF hydrate and its mechanism: Implication on hydrate-based H ₂ storage, Yin Zhenyuan [et al.] | 89 |

| | |
|---|-----------|
| A dual hydrate-based desalination and CO ₂ capture process: a Raman spectroscopy approach, Zafar Sadain [et al.] | 90 |
| Session 5: Hydrates and Astrophysics | 91 |
| Spectroscopic study of the methane hydrate at high pressure and temperature, Berni Selene [et al.] | 92 |
| Exploring the stability and new structures of gas filled ices up to Mbar pressures, Bove Livia Eleonora [et al.] | 93 |
| Methane Outgassing from Clathrate Hydrates on Titan: Partial Dissociation and Substitution Mechanisms, Gloesener Elodie [et al.] | 94 |
| Gas hydrates as indicators of cryomagmatic processes on Ocean worlds, Munoz-Iglesias Victoria [et al.] | 95 |
| Ammonia incorporation in methane clathrate within the subsurface ocean of Titan, Nozaki Shunsuke [et al.] | 96 |
| Gas separation and storage in mixed clathrate hydrates as studied by molecular simulations: Applications to astrophysical contexts, Patt Antoine [et al.] | 97 |
| Author Index | 98 |

Session 1: Fundamentals

Chair: Claire Pirim, Marco Zannotti, Bohui Shi

Thermodynamic criterion for predicting phase coexistence between two clathrate structures with different composition

Vincent Ballenegger¹, Olivia S. Moro^{1,2} and Nigel B. Wilding²

¹ *Université de Franche-Comté, CNRS, Institut UTINAM, F-25000 Besançon, France, vincent.ballenegger@univ-fcomte.fr*

² *HH Wills Physics Laboratory, Royal Fort, University of Bristol, Bristol BS8 1TL, U.K. nigel.wilding@bristol.ac.uk*

Transitions between different clathrate structures, e.g. structures I, II, H and T, have been observed in high-pressure diamond anvil cell experiments for several pure gas hydrates (CH₄, CO₂, N₂, Ar, Kr,)¹. Predicting theoretically the location of such a phase coexistence does not involve comparing solely the Gibbs free energy of the two coexisting clathrate phases because their compositions (gas mole fractions) are not identical. We derive a simple criterion for comparing the thermodynamic stability of two clathrate structures at a given temperature and pressure when one component is in excess in the experimental setup. This criterion can be used to determine the coexistence pressure in molecular simulations.

¹ J.S. Loveday and R.J. Nelmes, *Phys. Chem. Chem. Phys.*, 2008, **10**, 937–950

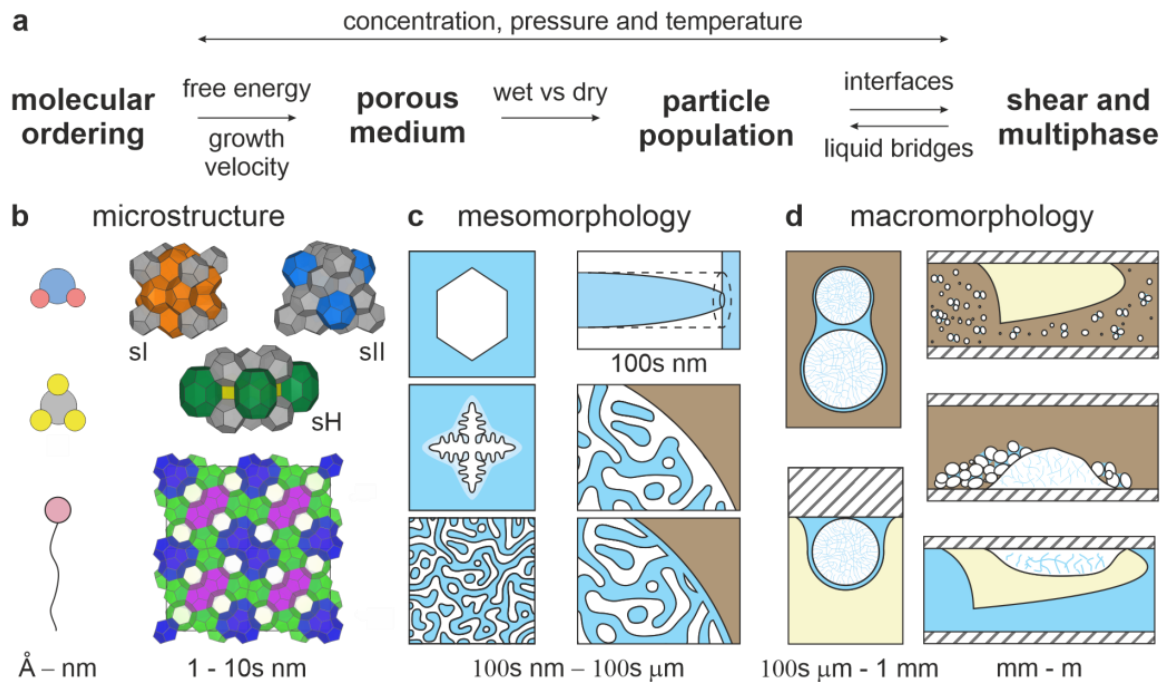
Mesomorphology of Clathrate Hydrates from Molecular Ordering

Carlos L. Bassani¹, Michael Engel¹, Amadeu K. Sum²

¹ Institute for Multiscale Simulation, Friedrich-Alexander-Universität Erlangen-Nürnberg, Cauerstraße 3, 91058 Erlangen, Germany

² Phases to Flow Laboratory, Chemical and Biological Engineering Department, Colorado School of Mines, Golden, Colorado 80401, United States

Whereas the thermodynamic equilibrium of clathrate hydrates is well described via the van der Waals and Plateeuw approach, the increasing concerns with global warming and energy transition requires extending the knowledge to non-equilibrium conditions in multiphase, sheared systems, in a multiscale framework. Potential macro-applications concern storage of carbon dioxide in the form of clathrates, and reduction of hydrate inhibition additives currently required in hydrocarbon production. We evidence porous mesomorphologies as key to bridge the molecular scales to macro applications of low solubility guests. We discuss the coupling of molecular ordering with the mesoscales, including (i) the emergence of porous patterns as a combined factor from the walk over the free energy landscape and 3D competitive nucleation and growth, and (ii) the role of molecular attachment rates in crystallization-diffusion models that allow predicting the timescale of pore sealing. In this talk, we give a perspective on how to use discrete models (molecular dynamics) to build continuum models (phase field models, crystallization laws, transport phenomena) to predict multiscale manifestations at a feasible computational cost. This talk is multidisciplinary and gathers several advances from correlated fields including ice, polymers, alloys, and nanoparticles.



Investigation of the crystallization kinetics of pure and mixed hydrates from mixtures of carbon dioxide and methane

Baptiste Bouillot¹, Madina Naukanova¹, Jean-Michel Herri¹, Onur Ozturk², Clement Roy³,
Shaiek Sadia⁴, Ornella Masi⁴

¹ Mines Saint-Etienne, Univ Lyon, CNRS, UMR 5307 LGF, Centre SPIN, F - 42023 Saint-Etienne -
France, bouillot@emse.fr

² CERG, 7 rue Lavoisier, 38800 Le Pont de Claix - France

³ Subsea7, 1 Quai Marcel Dassault, 92150 Suresnes - France

⁴ SAIPEM SpA, Via Toniolo, 1, 61032 Fano (PU) - Italy

The objective of this investigation is to obtain experimental data on induction times and formation kinetics of clathrate hydrates from mixtures of carbon dioxide and methane in water.

The main motivation for such study is to evaluate the impact of carbon dioxide as an impurity in methane and, conversely, the impact of methane as an impurity in the carbon dioxide atmosphere when hydrates can form. Three symmetrical systems were therefore considered: pure gases, a highly concentrated system (molar ratios of 95:5), and a less concentrated one (75:25).

The hydrate formation procedure involved crystallization in a pressurized batch reactor (fixed volume and stirring rate). Different driving forces were used, but for each gas mixture, a test condition with a driving force of $\Delta p \approx 18$ bars was performed. To evaluate this driving force before filling the reactor, a thermodynamic model based on van der Waals and Platteeuw approach was used. Temperature, and pressure were recorded online during hydrate formation, and gas compositions were analyzed by means of gas chromatography. The hydrate volume and composition were determined from mass balance calculations using water concentration analysis (using LiNO_3 as tracer in the aqueous solution).

This procedure makes it possible to obtain the induction time, the water conversion ratios, and the volume of hydrates throughout the hydrate formation stage.

The results showed that the induction time is generally rapid, with nucleation occurring within two hours. However, the presence of a significant amount of methane as an impurity can mask this first event with a low nucleation rate. In such case, the time needed to reach the end of the crystallization stage is about one week long. With a higher driving force, such as 24 bars, this period can extend up to three weeks. In addition, the higher the methane concentration, the slower the conversion of water at the start of crystallization.

Thermodynamic modelling for equilibrium and flash calculations proved to be fairly accurate, predicting water conversion ratios and the mass of water converted into hydrates with less than 10% error. However, this error increases for tests with rich- CO_2 gas mixtures. Therefore, compared to methane, carbon dioxide content has probably a greater influence on hydrate formation kinetics

This work has been supported by CITEPH 2022-19-1 Hydrakine Project.

Investigating Deuterated Clathrate Hydrates as Novel Moderator Material for Very Cold Neutrons – A Neutron Scattering Study

Valentin Czamler¹, Richard Wagner², Oliver Zimmer¹
¹ *Institut Laue-Langevin, Grenoble, email: vczamler@ill.fr*
² *Laboratoire Léon Brillouin, CEA Saclay, Gif sur Yvette*

Very cold neutrons (VCN) cover a wide spectral range within the long-wavelength tail of typical sources for cold neutrons, with energies below 1 meV down to few hundreds of neV, the domain of ultracold neutrons (UCN). Clathrate hydrates exhibit intrinsic properties that make them suited as moderators in novel, more intense sources of VCN. Such sources have the potential to enhance existing neutron scattering techniques, for example, small angle neutron scattering (SANS) in terms of spatial resolution, as well as time of flight (TOF) and neutron spin echo (NSE) spectroscopy in regard to energy resolution. In particle physics, higher VCN intensities would increase the sensitivity of experiments that employ beams of slow neutrons. Examples are the search for neutron-antineutron oscillations or in-beam searches for a static neutron electric dipole moment (EDM) [1].

The efficacy of clathrate hydrates for neutron moderation is attributed to the localized low-energy modes of the entrapped guest molecules. These facilitate down-scattering of neutrons, which is not restricted by any dispersion relation, allowing an efficient thermalization even at lowest neutron temperatures. Of particular interest are hydrates hosting dioxygen (O₂) and tetrahydrofuran (THF) as guest molecules. THF provides a broad excitation spectrum, while dioxygen provides an additional path for neutron slowdown by exploiting the zero-field splitting of its magnetic triplet ground state [2].

In our contribution, we report the status of the experimental campaign investigating the structure and low-energy dynamics of these hydrates by means of neutron scattering. This campaign is part of a collaborative effort to develop a high-intensity cold neutron source at the European Spallation Source (ESS) [3]. Previous studies reported measurements of the neutron dynamic structure factor $S(q, \omega)$ of methane and THF clathrate hydrates [4]. These data, however, have been reported in arbitrary units, which cannot be used for quantitative predictions of the performance of clathrate hydrate moderators by simulations. We present, in absolute units, the results of measurements of the temperature-dependent dynamic structure factor of fully deuterated THF hydrates [5] and binary hydrates hosting THF and dioxygen, carried out at the Panther and IN5 instruments at the ILL. These measurements served as input to develop respective NCrystal [6] scattering kernels, within the HighNESS project [3].

Additionally, we report the results of our study on the manufacturing of binary clathrate hydrates hosting THF and molecular oxygen. We demonstrated, with neutron diffraction at the ILL instrument D20, that binary hydrates are formed from fine powders of THF hydrates. We were not only able to confirm the CS-II structure, but also to determine the cage occupancy and thermal expansivity. The latter shows interesting behavior at low temperatures, due to the low excitation energies of the localized modes. These studies are complemented by TOF transmission data in the cold and very cold spectra through samples of deuterated THF hydrates, performed using the PF2-VCN and PF1B beamlines at the ILL. From these data, we were able to compute the total neutron cross section and the mean free path of these hydrates, which are transport parameters that are critical for accurate simulations of neutron moderation to the VCN energy range.

References

- [1] N. Rizzi et al., *Nuc. Instr. & Methods A*, 1062, 169215 (2024).
- [2] O. Zimmer, *Phys. Rev. C* 93, 035503 (2016).
- [3] V. Santoro et al., *arXiv:2309.17333v3* (2024).
- [4] H. Conrad et al., *Physica B* 350, e647 (2004).
- [5] V. Czamler et al., *EPJ Web of Conf.*, 286, 5004 (2023).
- [6] X.-X. Cai, T. Kittelmann, *Comput. Phys. Commun.*, 246, 106851 (2020).

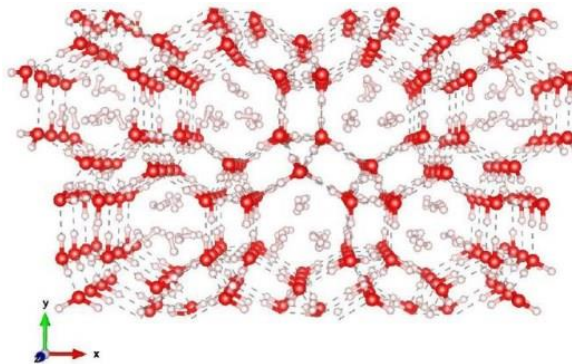
Emptied hydrates as advanced functional materials: from a scientific curiosity to hydrogen storage applications

Leonardo del Rosso¹, Daniele Colognesi¹, Milva Celli¹

¹ *Consiglio Nazionale delle Ricerche - Istituto di Fisica Applicata "Nello Carrara", Sesto Fiorentino, Italy, l.delrosso@ifac.cnr.it*

The investigation of the phase diagram of the solid mixture of water and molecular hydrogen at high pressure has been particularly prolific and associated with exciting discoveries. Several solid stoichiometric and non-stoichiometric phases of this mixture have been characterized in the latest years [1], some of which, being metastable at ambient pressure and low temperature (77 K), can be recovered and handled in laboratory. Among these, the so-called C_0 phase led to the discovery, by out-diffusion of hydrogen molecules at about 130 K, of a metastable phase of ice, named afterwards ice XVII [2]. Surprisingly, this low-density solid is highly porous and presents accessible spiralling channels where hydrogen molecules can be reversibly hosted in an essentially one-dimensional geometry. Later, similar properties were also observed by dosing both ice XVI [3] and ice XVII [4] with different types of gases, further enhancing the fundamental and applicative interest in these low-density materials. In this talk we report our studies concerning the structural and dynamical characterization of the C_0 hydrate and its emptied counterpart, i.e., ice XVII [5,6], as well as the dynamics of the gas molecules confined in the ice XVII framework [7], mainly performed through Raman and neutron scattering experiments. We will also discuss its possible use as an innovative and fully “green” material for hydrogen storage [8].

- [1] U. Ranieri et al., PNAS 120, e2312665120 (2023).
- [2] L. del Rosso et al., Nat. Commun. 7, 13394 (2016).
- [3] W. F. Kuhs et al., J. Phys. Chem. Lett. 9, 3194 (2018).
- [4] M. Catti et al., Phys. Chem. Chem. Phys. 21, 14671 (2019).
- [5] L. del Rosso et al., Phys. Rev. Mat. 1, 065602 (2017).
- [6] L. del Rosso et al., Chem. Phys. 544, 111092 (2021).
- [7] L. del Rosso et al., J. Chem. Phys., under review (2024).
- [8] L. del Rosso et al., Challenges 8, 3 (2017).



Perspective view of the H₂-refilled ice XVII crystal structure

Effect of perchloric acid on the thermodynamics of tetrahydrofuran and mixed methane/tetrahydrofuran hydrates

Dounya FRAH^{1,2}, Emilie BORDES¹, Anne SINQUIN¹, Arnaud DESMEDT³

¹ IFP Energies nouvelles, Rueil-Malmaison, France, dounya.frah@ifpen.fr

² Groupe Spectroscopie Moléculaire – GSM, ISM-CNRS, Talence, France, sophie.sobanska@u-bordeaux.fr

³ Laboratoire Léon Brillouin – LLB, CEA-CNRS, Gif sur Yvette, France, llb-sec@cea.fr

Hydrates form when at least one molecular species (guest) co-crystallizes with water molecules (host), creating aqueous cages where guest molecules are encapsulated [1]. In recent decades, there has been growing interest in ionic hydrates, which involve the inclusion of ionic species, driven by their potential technological applications and unique physicochemical properties [2]. Introduction of ionic guest molecules (such as bases, strong acids, or quaternary ammonium salts) results in the formation of water substructures containing ionic defects, as counterions are incorporated within the water framework. These chemical defects contravene the ice rule, altering the intrinsic properties of hydrates [3]. Research investigates the impact of acidic defects on the thermodynamic properties of hydrates particularly on tetrahydrofuran (THF) hydrates according to the following stoichiometry: $(1-\alpha)$ THF· α HClO₄·17H₂O with α ranging from 0 to ½ [3]. It has been observed that beyond this inherent limitation, a multiphase regime is observed in the formation of hydrates (a mixture of type I and type II). Furthermore, investigations on hydrogen hydrates were conducted leading to the promotion of molecular hydrogen insertion within the hydrate structure. Moreover, the hydrogen diffusion coefficient was found to be improved by a factor of 2 thanks to the acidic additive [4]. Therefore, it was interesting to observe the effect of perchloric acid on other gases besides hydrogen, such as methane, for example. In this study, we have focused our work on the effect of perchloric acid on THF Structure II atmospheric hydrates and on mixed hydrates stabilized at high pressure (70 bar) by both THF and methane. The effect of the perchloric acid/THF ratio was explored using a differential scanning calorimeter. THF hydrate and mixed methane/THF hydrates with perchloric acid were characterized at dissociation: stability conditions of the studied mixed hydrates, and enthalpies of dissociation were determined. In the presence of acid-type additives, new species were found that dissociate at lower temperature with a smaller enthalpy of dissociation. The stability displacement is correlated with α . Addition of perchloric acid causes the ice dissociation peak's disappearance, the new species (THF/ion or methane/THF/ion) are preferentially formed.

Keywords: Tetrahydrofuran hydrates, Methane hydrates, Perchloric acid, Differential Scanning Calorimetry

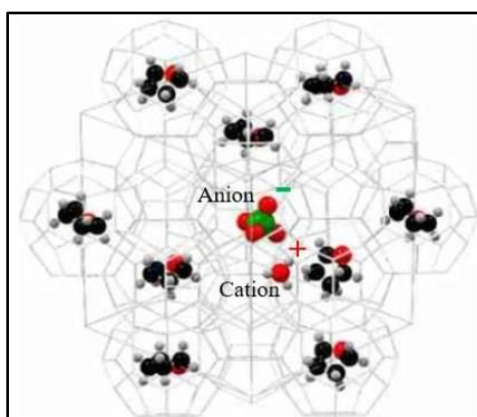


Figure: Representation of the THF hydrate formed with acidic additives [3].

[1] Sloan, E. D.; Koh, C. A. Clathrate Hydrates of Natural Gases, 3rd ed.; Taylor & Francis-CRC Press: Boca Raton, FL, 2008. [2] Shin, K.; Cha, M.; Choi, S.; Dho, J.; Lee, H. Discrete Magnetic Patterns of Nonionic and Ionic Clathrate Hydrates. *J. Am. Chem. Soc.* 2008, 130, 17234–17235. [3] Desmedt, A.; Martin-Gondre, L.; Nguyen, TT.; Petuya, C.; Barandiaran, L.; Babot, O.; Toupance, T.; Grim, RG.; Sum, AK. Modifying the flexibility of water cages by co-including acidic species within clathrate hydrate. *J. Phys. Chem. C* 2015, 119, 8904–8911. [4] Nguyen, TT.; Pétuya, C.; Talaga, D.; Desmedt, A. Promoting the Insertion of Molecular Hydrogen in Tetrahydrofuran Hydrate With the Help of Acidic Additives. *Front. Chem.* 2020, 8:550862.

The Impact of Alcohol and Ammonium Fluoride on Pressure-Induced Amorphization of Cubic Structure I Clathrate Hydrates

Lilli-Ruth Fidler¹, Paul Posch¹, Johannes Klocker², Thomas S. Hofer², Thomas Loerting¹

¹ Institute of Physical Chemistry, University of Innsbruck, thomas.loerting@uibk.ac.at

² Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck, t.hofer@uibk.ac.at

We have investigated pressure-induced amorphization (PIA) of an alcohol clathrate hydrate (CH) of cubic structure type I (sI) in the presence of NH₄F utilizing dilatometry, X-ray powder diffraction and molecular dynamics simulations^[1]. This unusual CH with ethanol and methanol acting as guests and NH₄F incorporated into the host lattice in the manner of a solid solution has been first synthesized by Shin et al.^[2]. It represents a breakthrough in the synthesis of alcohol-containing CHs^[2,3], eliminating the requirement of a hydrophobic helper guest.

PIA of this sI CH occurs at 0.98 GPa at 77 K, while other CHs of the same structure type, such as methane hydrates, only amorphize above 2 GPa^[4,5]. The amorphized CH in our study also shows a remarkable resistance against crystallization upon decompression. While amorphized sI CHs could not be recovered previously at all, we are able to recover the CH to ambient pressure and characterize it *ex situ*. By contrast to sII CHs the recovery of the amorphized CHs to ambient pressure does not even require a high-pressure annealing step^[6,7]. Recovery without any loss of amorphicity is possible at 120 K and below. Further, PIA rather than polymorphic transitions takes place upon compression up to unusually high temperatures of 140 K. At 140 K the sI CH reaches the highest degree of amorphicity.

Reasons for this unique behavior are suggested from molecular dynamics simulations, which suggest that polar alcoholic guests induce cage deformation at lower pressure than non-polar guests. This is due to the formation of weak hydrogen bonds between guest and host lattice. The substitution of NH₄F into the host-lattice on the other hand stabilizes the collapsed state more than the crystalline state, thereby enhancing the collapse kinetics and lowering the pressure of collapse.

[1] L.-R. Fidler, P. Posch, J. Klocker, T. S. Hofer, T. Loerting, *J. Chem. Phys.* **2024** (submitted for publication).

[2] K. Shin, I. L. Moudrakovski, C. I. Ratcliffe, J. A. Ripmeester, *Angew. Chemie* **2017**, *129*, 6267–6271.

[3] K. Shin, I. L. Moudrakovski, M. D. Davari, S. Alavi, C. I. Ratcliffe, J. A. Ripmeester, *CrystEngComm* **2014**, *16*, 7209–7217.

[4] C. A. Tulk, D. D. Klug, J. J. Molaison, A. M. Dos Santos, N. Pradhan, *Phys. Rev. B - Condens. Matter Mater. Phys.* **2012**, *86*, 1–8.

[5] N. Noguchi, Y. Shiraishi, M. Kageyama, Y. Yokoi, S. Kurohama, N. Okada, H. Okamura, *Phys. Chem. Chem. Phys.* **2023**, *25*, 22161–22170.

[6] Y. Suzuki, *Phys. Rev. B - Condens. Matter Mater. Phys.* **2004**, *70*, 1–4.

[7] M. Bauer, D. M. Töbrens, E. Mayer, T. Loerting, *Phys. Chem. Chem. Phys.* **2011**, *13*, 2167–2171.

Unraveling the effect of double occupancy in N₂ gas hydrates

Ludovic Martin-Gondre¹, Maxime Legrand¹, Claire Pétuya², Cyrielle Métais^{1,2,3}, Jacques Ollivier³, Arnaud Desmedt^{2,4}

¹Institut UTINAM, UMR6213 CNRS – Univ. Franche-Comté, Besançon, France ²Institut des Sciences Moléculaires (ISM), UMR5255 CNRS – Univ. Bordeaux, France ³Institut Laue Langevin (ILL), Grenoble, France

⁴Laboratoire Léon Brillouin (LLB), UMR12 CEA-CNRS, Gif sur Yvette, France

At a fundamental level, the nano-structuration of gas hydrates confers on these materials specific physico-chemical properties. The understanding of their molecular interactions plays a key role in the future developments – requiring to combine advanced experimental and computational approaches. Density functional theory (DFT) method is one of the most fundamental approaches in computer simulations and is particularly well suited to the study of periodic system as clathrate hydrates.

In this work, DFT calculations were performed to disentangle the effect of double occupancy in large N₂ clathrate hydrates cages. Indeed, N₂ gas hydrates can form into one type (sI structure) and transform into another type (sII structure) within a few days, as revealed by means of time-dependent and in situ neutron diffraction experiments [1]. This structure change is associated with the ability of gas hydrates to catch two guest molecules in the sII structure. In previous work, we showed that binding energy, i.e. the interaction energy between N₂ and water molecules, is lower for sII structures compared to sI, confirming the fact that the sII structure is favored with regard to double occupancy [2].

The poster will review these recent results and will focus on new findings regarding the effect of pressure on the energetic properties in N₂ clathrate hydrates. Convex hull diagrams will be used to discuss the stability of structures under pressure. In addition, preliminary results on the kinetic aspects of double occupancy will be presented thanks to a coupling of DFT and Kinetic Monte Carlo calculations.

[1] C. Pétuya, F. Damay, D. Talaga and A. Desmedt, J. Phys. Chem. C 121 (2017) 13798.

[2] C. Métais, C. Pétuya, S. Espert, J. Ollivier, L. Martin-Gondre and A. Desmedt, J. Phys. Chem. C 125 (2021) 6433.

Relative thermodynamic stability of gas hydrate structures from Lattice-Switch Monte Carlo simulations

Olivia S. Moro^{1,2}, Vincent Ballenegger¹ and Nigel B. Wilding²

¹ Université de Franche-Comté - , France.

olivia.moro@univ-fcomte.fr

vincent.ballenegger@univ-fcomte.fr

² HH Wills Physics Laboratory, Royal Fort, University of Bristol, Bristol BS8 1TL, U.K.

nigel.wilding@bristol.ac.uk

Experimental studies have reported structural transitions between several pure gas (CH₄, Ar, ..) hydrate structures at high pressure (such as structure I, II or H)¹. Having a cost-effective numerical method to compute coexistence curves is an advantage especially in case where experimental setup can't reproduce conditions in which we are interested.

To compute the coexistence curve for a specific gas hydrate, one has to study the relative stability between two structures (structure II and H for instance). The structure that is thermodynamically stable, for a given pressure, temperature is the one with the lowest Gibbs free energy G . The Lattice-Switch Monte Carlo (LSMC)^{2,3} method offers a direct way to compute the free energy *difference* between two crystalline structures. In this method, a single (biased) Monte Carlo simulation samples the two crystalline structures and the free energy difference ΔG is obtained from the ratio of the probability of the system being found in the each of the two phases. LSMC has the advantages of focussing on the difference ΔG (rather than on absolute free energies), of providing a straightforward estimate of the uncertainty in ΔG and of properly accounting for volume fluctuations since the calculations are performed at constant pressure. A constraint is that the number of molecules must be equal for the two crystalline structures considered. We show that the LSMC method can be applied, despite this constraint, to compute free energy differences between gas hydrates structures (e.g. structures I, II and H). We show how to obtain ΔG for gas hydrate at real occupancy at a given pressure and temperature. We compare our results with the existing literature in the case of methane hydrate.

¹ J.S. Loveday and R.J. Nelmes, *Phys. Chem. Chem. Phys.*, 2008, 10, 937–950

² A. D. Bruce et al., *Phys Rev E* 61, 906 (2000)

³ T. Underwood et G. Ackland. *Comput Phys Commun.* 216 (2017)

Understanding the Influence of Nano-Bubbles on CO₂ Hydrate Growth: An Investigation from Experimental and Molecular Dynamics Simulation

Parisa Naeiji¹, Mengdi Pan², Niall J. English³

School of Chemical and Bioprocess Engineering, University College Dublin, Belfield, Dublin, Ireland

¹*parisa.naeiji@ucd.ie*, ²*mengdi.pan@ucd.ie*, ³*niall.english@ucd.ie*

Gas hydrate growth in contact with nanobubbles is an interesting research area with potential applications in energy production and storage. With the presence of nanobubbles, the growth and stability of gas hydrates can be largely influenced. Nanobubbles provide a large surface area for gas absorption which may enhance the interaction between gas molecules and water, promoting the formation of gas hydrates. Nanobubbles can facilitate the transfer of gas molecules to the water phase, thus contributing to the saturation of the water with gas, promoting gas hydrate nucleation and growth. The specific characteristics of the nanobubble surface can also influence the kinetics of hydrate growth. Research in this area typically involves experimental studies, molecular dynamics (MD) simulations, and mathematical modeling to understand the complex processes at the nanoscale. This work investigates the effect of CO₂ nanobubbles on the hydrate growth through both laboratory works and MD simulations.

Experiments started with the dissociation of CO₂ hydrates for the generation of CO₂ nanobubbles. The existence of bulk nanobubbles were confirmed and characterized using Dynamic Light Scattering after a complete melting of the hydrates. To investigate the hydrate growth process, the completely melted solution was pressurized with CO₂ gas at a pressure and temperature condition within the hydrate equilibrium. The system was continuously monitored for over 4 hours to gauge a final pressure drop, from which the hydrate formation kinetics was estimated. CO₂ hydrate formation with deionized water under identical condition was selected as a reference. In addition, CO₂ nanobubbles generated from a sustained electric field were also used to further study the effect of nanobubble size concentrations on the hydrate formation process. The preliminary results suggest a significant promoting effect of bulk nanobubbles on hydrate formation kinetics. MD simulations revealed the mechanism of the promoting effect on a molecular scale. The results show that nanobubbles can form as a result of CO₂ release into the liquid water phase due to hydrate dissociation, which supersaturates liquid water. The simulation was done for the different CO₂ concentrations in the solutions. During the growth process, the size and shape of nano-bubbles changed, and they were getting smaller. The interaction between water and CO₂ molecules also increased as the hydrate surface absorbed the gas molecules from the solution and consumed them to form new hydrate cavities. Therefore, CO₂ molecules have less preference to interact with each other and thus the gas clusters were shrinking during the simulation. The nanobubbles remained in the vicinity of the hydrate interface and provided CO₂ for hydrate growth. When the bubble becomes so small that it is no longer stable, it collapses, creating a large local concentration of CO₂ in the aqueous phase, further facilitating hydrate growth. The results showed that the lowest growth rate belonged to the system with the highest amount of CO₂. On the other hand, the system with the lowest amount of CO₂ could not complete the hydrate growth process due to the reduction or lack of CO₂ content in the system. Therefore, it can be stated that a large nano-bubble may inhibit the hydrate formation, or the process may be hindered by the absence of gas molecules in the solution. Thus, it was found that a solution with 12.5 mol% CO₂ and a nano-bubble size of around 12.5 Å can promote hydrate growth in the present work.

Promoting effect of a natural peptide on methane-hydrate formation: insights from experiments and molecular-dynamics simulations

Bastien Radola,^{1,2} Mengdi Pan,¹ Niall J. English,¹ Christopher C.R. Allen,²
¹ School of Chemical and Bioprocess Engineering, University College Dublin, Dublin 4, Ireland
² School of Biological Sciences, Queen's University Belfast, Belfast BT9 5DL, Northern Ireland

Methane hydrates are the most abundant clathrates found in the environment, predominantly in the permafrost and marine continental-shelf regions. As such, they constitute an energy resource and a concern for climate change, as well as a potentially significant source of carbon for the microbial communities living in the same environments. However, relatively little is known about the way that these microorganisms interact, if at all, with methane hydrate deposits. A recent study revealed that a porin produced by a marine methylotroph (*Methylophaga aminisulfidivorans*) was found to promote hydrate formation in conditions mimicking that of the seafloor [1]. A specific peptide sequence (TAFDGGS) was shown to be responsible, at least partially, for this behavior [2]. However, the exact physicochemical mechanisms underlying such effects remain unclear.

Our research employed a dual methodology, integrating experimental procedures with molecular dynamics simulations to shed light on how naturally-occurring peptides can influence methane-hydrate formation. First, laboratory experiments were conducted to observe the kinetics of methane-hydrate formation in the presence of the selected natural peptide. Experiments using the same procedure were repeated with sodium dodecyl sulfate (SDS), a known hydrate promoter, as well as deionized water, serving as a reference. In parallel, molecular dynamics simulations were carried out on systems composed of liquid water and methane, with or without the presence of a peptide. The evolution of the hydrate content in the simulation box was computed at various methane concentrations. The in-depth analysis of the interactions between the peptide and water and methane molecules provided molecular-level insights on how the former can influence the nucleation and growth of methane hydrate clusters. Our results experimentally confirmed that the natural peptide exhibits a distinctive promoting effect on the formation kinetics of methane hydrate. However, the initially proposed mechanism of a promoting effect achieved by providing more nucleation sites was ruled out. Instead, our results suggest a more complex bio-catalytic effect on hydrate kinetics.

This study hints at a potential for peptides as eco-friendly alternatives to traditional chemical promoters in methane hydrate research and provides valuable insights into the design of efficient and sustainable promoters. More fundamentally, this study lays a solid foundation for our understanding of the interactions between peptides and hydrates in nature and paves the way for further research on the role of bio-molecules and microorganisms on methane hydrate deposits.

References

- (1) Ghaani, M. R.; Allen, C. C. R.; Young, J. M.; Prithwish, K. N.; Shamsudee, U. D.; Skvortsov, T.; English, N. J. *Geomicrobiol. J.* **2020**, *37*, 279-286
- (2) Ghaani, M. R.; Allen, C. C. R.; Skvortsov, T.; English, N. J. *J. Phys. Chem. Lett.* **2020**, *11*, 5068–5075

Flue gas and desalination from seawater : thermodynamics and kinetic influence of salt and cooling rate

Angsar Serikkali¹, Jérôme Douzet¹, Jean-Michel Herri¹, Baptiste Bouillot¹

¹ Mines Saint-Etienne, Univ Lyon, CNRS, UMR 5307 LGF, Centre SPIN, F - 42023 Saint-Etienne, bouillot@emse.fr

Hydrate-based technologies for carbon capture and desalination are a hot topic in the hydrate community today. Although many efforts have been made to capture carbon from flue gases or to desalinate seawater from CO₂ and cyclopentane hydrates, very few studies have focused on the thermodynamic behaviour of both processes at the same time.

Firstly, thermodynamic equilibrium was studied experimentally (pressure range: 20 to 65 bar). A mixture of 15%/85%mol CO₂ and N₂ respectively was considered. Cyclopentane was used as a promoter because it can significantly reduce the equilibrium pressure (or increase the equilibrium temperature). In addition, it can be recovered after hydrate dissociation because it is not very miscible in water. Figure 1 shows the equilibrium curve compared to systems without cyclopentane, seawater or any additives.

Next, the kinetics of hydrate formation were observed. The evolution of pressure/temperature as a function of time was recorded, and two cooling rates for crystallisation were used. In addition, a correlation based on previous work was used to estimate the amount of hydrate formed.

The main results showed that: the introduction of 3.5 wt% NaCl into the system significantly slowed down the crystallisation process; the cooling rate did not significantly affect the final state of the system after crystallisation.

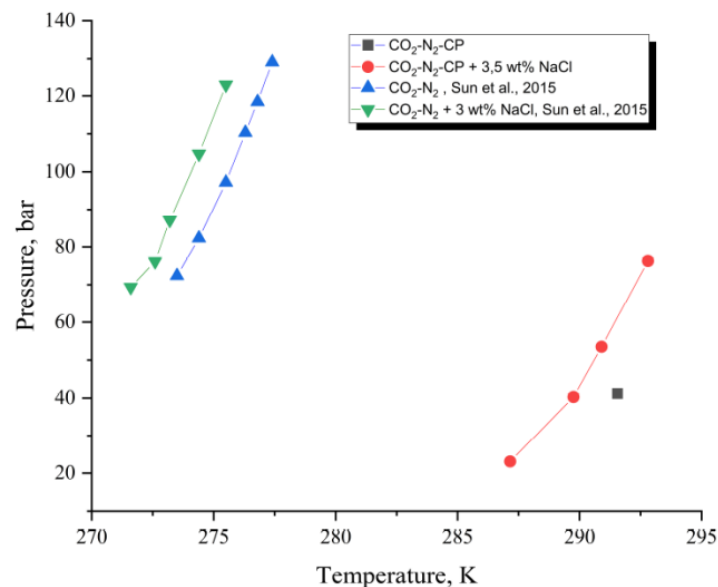


Figure 1. Thermodynamic data associated with the dissociation of mixed CO₂-N₂-CP hydrates in seawater are presented, juxtaposed with the findings from Sun et al. (2015).

Investigation of [BMIM]FeCl₄ ionic liquid as hydrate promotor for carbon capture from seawater

Angsar Serikkali¹, Jérôme Douzet¹, Jean-Michel Herri¹, Baptiste Bouillot¹

¹ Mines Saint-Etienne, Univ Lyon, CNRS, UMR 5307 LGF, Centre SPIN, F - 42023 Saint-Etienne, bouillot@emse.fr

A few years ago, iron-based ionic liquids were studied as kinetic promoters for gas hydrates (Liu et al. 2021). As hydrate formation kinetics is a well-known problem for the development of hydrate-based technologies, the idea behind this study is to validate, or invalidate, the use of [BMIM]FeCl₄ ionic liquid for carbon capture from seawater..

The work comprises three stages: the influence of NaCl concentration on the liquid-liquid equilibrium of brine and ionic liquids; the thermodynamic equilibrium of CO₂ hydrates in the presence of seawater and ionic liquids; and the kinetics of hydrate formation. The first stage provided the two-phase ternary diagram in the vicinity of the expected industrial conditions. Next, the kinetic constants for the gas to liquid and liquid to hydrate mass transfer were estimated..

The results showed a thermodynamic inhibition effect for CO₂ hydrates (as expected by the addition of electrolytes to the aqueous solution), see Fig. 1. However, from a kinetic point of view, the results showed that there was no significant improvement. Therefore, the use of [BMIM]FeCl₄ did not prove to be a good overall promoter.

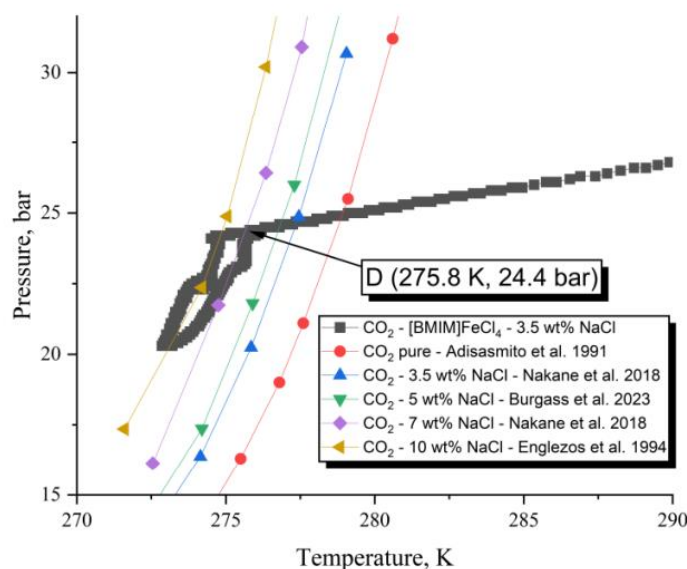


Fig. 1. PT curve of CO₂ hydrate formation and dissociation in the presence of 5v% [BMIM]FeCl₄ and 3.5 wt% NaCl in comparison with the literature data.

Fa Ping Liu, Ai Rong Li, Jie Wang, and Ze Dong Luo. Iron-based ionic liquid ([BMIM][FeCl₄]) as a promoter of CO₂ hydrate nucleation and growth. *Energy*, 214:119034, 2021.

Experimental determination of stable and metastable equilibria involving CO₂ hydrate, ice, liquid water and gaseous CO₂

Abdelhafid Touil^{1,2} and Daniel Broseta²

¹ *Direction Centrale de Recherche et Développement, Sonatrach, 35000 Boumerdes Algeria*

abdelhafid.touil@sonatrach.dz

² *LFCR, UMR 5150 CNRS-Université de Pau et des Pays de L'Adour, 64000 Pau France*

daniel.broseta@univ-pau.fr

We experimentally determine the three-phase equilibrium lines in the temperature-pressure domain between CO₂ hydrate (H), vapor (V) and liquid water (L_w) and between ice (I), V and L_w, that meet at the lower quadruple point Q₁. The experimental procedure consists in monitoring in a thin glass capillary the disappearance of the hydrate or ice phase near the meniscus between the aqueous and vapor phases when temperature or pressure are varied slowly. This monitoring is carried by means of an optical microscope used in the transmission and/or polarized modes, the latter mode being convenient for observing hexagonal ice. We also determine the metastable extension of the three-phase line L_w-H-V for temperatures and pressures below those of Q₁, where the gas hydrate coexists with vapor and supercooled liquid water (L_w^{*}). This extension exhibits a Clausius-Clapeyron behavior similar to that of the stable (i.e., L_w-H-V) part, meaning similar dissociation behavior, whether the hydrate melts to a supercooled liquid water state or to liquid water.

CO₂ sequestration via gas hydrates: Raman and morphological characterization of CO₂, CH₄ and CO₂/CH₄ gas hydrates

Marco Zannotti¹, Marco Minicucci² and R. Giovannetti¹

¹ School of Science and Technology, Chemistry Interdisciplinary Project (CHIP), University of Camerino, Via Madonna delle Carceri, 62032 Camerino (MC)

² School of Science and Technology, Physics Division, University of Camerino, Via Madonna delle Carceri, 62032 Camerino (MC)

marco.zannotti@unicam.it

The most important and promising strategies to collect CH₄ are related to the CO₂ replacement that allows permanent storage of CO₂, as reducing greenhouse gas without additional energy ¹.

In the context of the PRIN2017 Project “Methane recovery and carbon dioxide disposal in natural gas hydrate reservoirs”, some marine sediment samples that contained NGHs, were chemically analyzed to obtain indications for the synthetic reproduction of GHs in laboratory. Different CH₄, CO₂ and CO₂/CH₄ GHs, were ex situ analyzed by using Raman-spectroscopy and morphological characterized by low-temperature SEM (LTSEM) measurements. The chemical composition in seawater of marine sediments, as well as the physical properties and chemical composition of soils, influence the phase behavior of NGHs by disturbing the H-bond network in the water-rich phase before GH formation. The salts influence the formation of NGHs and their nucleation occurs preferentially in a region with low ions concentration; for these reasons, the investigation about the chemical composition of seawater containing NGHs is very important to obtain useful data for the comprehension of their formation mechanisms in the natural environment. To this purpose, water inside some marine sediment samples that contained natural GHs, sampled in the Antarctic Peninsula during the summer of 2003–2004 by Italian National Antarctic Research Program², were chemically analyzed (by ICP-MS and ionic chromatography) to obtain the indications for the synthetic reproduction of GHs.

The application of the replacement strategies in NGHs reservoirs, always leads to the formation of “mixed” hydrates, whose mechanical and chemical properties are different from those of pure CH₄ and CO₂ hydrates³. In this study, the process of the replacement of CH₄ with CO₂ molecules into hydrates was described at a molecular level by studying with Raman measurements different laboratory reproduced GHs; the obtained data permitted to evaluate properties and behavior of the different GHs through the study of fingerprint of host molecules and of water OHs bands. Specifically, the results showed that the CO₂ hydrates showed a less ordered structure in the presence of sand but however, thanks to the interaction between water and silanol groups of sand particles, their stability was maintained with the variation of temperature, favoring the expansion of the cages that was highlighted by the Raman shifts of the CO₂ Fermi diad. The observation of the water OHs bands, interpreted by S_D indices⁴ showed that these parameters correlated perfectly with the increase of temperature and also provided information about the characteristics of water inside GHs, showing that the least ordered water structure was present on CO₂GHs in the presence of sediments, while the most ordered one was that of (CH₄/CO₂)GHs.

The LTSEM analysis highlighted clear differences in the micro-shapes between the various GHs samples, displaying changes in the surface morphology related to specific hydrate composition.

1. A. Hassanpouryouzband, E. Joonaki, M. V. Farahani, S. Takeya, C. Ruppel, J. Yang, N. J. English, J. M. Schicks, K. Edlmann, H. Mehrabian, Z. M. Aman, B. Tohidi *Chem. Soc. Rev.*, 49 (2020) 5225-5309.

2. U. Tinivella, F. Accaino, B. Della-Vedova, *Geo-Mar. Lett.* 28 (2008) 97–106.

3. R. Giovannetti, A. M. Gambelli, A. Rossi, B. Castellani, M. Minicucci, M. Zannotti, A. Nicolini, F. Rossi, *J. Mol. Liq.* 368 (2022) 120739.

4. I. Đuričković, M. Marchetti, R. Claverie, P. Bourson, J-M. Chassot, MD. Fontana *Appl. Spectrosc.* 64, 8 (2010) 853-857.

Molecular dynamics simulations of the effect of anti-agglomerant and wax molecular on methane hydrate growth

Yumo /Zhu¹, Bohui /Shi^{1,2,*}, Shangfei /Song¹, Jinhao /Sui¹, Lihao /Liu¹, Najia /Liao¹, Haiyuan /Yao³, Jing /Gong¹

¹ National Engineering Research Center of Oil and Gas Pipeline Transportation Safety/ MOE Key Laboratory of Petroleum Engineering/ Beijing Key Laboratory of Urban Oil and Gas Distribution Technology/ State Key Laboratory of Natural Gas Hydrates, China University of Petroleum-Beijing, Beijing, annaplay@163.com

² College of Carbon Neutral Energy, China University of Petroleum-Beijing, Beijing, bh.sh@cup.edu.cn

³ Key Lab of Deepwater Engineering, CNOOC Research Institute, Beijing, yaohy2@cnooc.com.cn

* Corresponding author(s): Bohui Shi (bh.shi@cup.edu.cn)

In oil-dominated systems, anti-agglomerants (AAs) are often used to retard hydrate aggregation to reduce the risk of hydrate plugging. However, the effect of AAs on hydrate growth has rarely been studied. When the system contains wax, the amphiphilicity of AAs may make the hydrate growth process in the system more complicated. In this work, molecular dynamics (MD) simulations were applied to investigate the effect of AA surfactant molecules (Span60) and wax molecules (Straight chain alkanes $C_{32}H_{66}$) on methane hydrate growth. The simulation case setup and critical moments are plotted in Figure 1. The results show that the amount of hydrate growth is minimized in Case I and a water film always exists between the hydrate phase and the oil phase. Case II has the fastest hydrate growth rate and the water film disappears creating the largest amount of hydrate growth. In Case III, the hydrate growth before Span60 adsorption is the same as that of Case I, and the amount of hydrate formation increases after adsorption. When Span60 and wax molecules are present at the same time, the hydrate growth rate is comparable to Case II, but the wax adsorption side water film still exists, making the lower amount of hydrate growth than that of Case II. This suggests that AA surfactant (Span60) promotes hydrate growth by converting the water film between the hydrate phase and oil phases mainly through its adsorption behavior at the oil-water interface. The presence of wax molecules forms co-crystals with Span60, which creates a spatial site-blocking effect on the mass transfer of methane molecules and alleviates the promoting effect. This finding provides a theoretical basis for the better application of AA in hydrate prevention and control in wax-containing oil-water systems from a microscopic perspective.

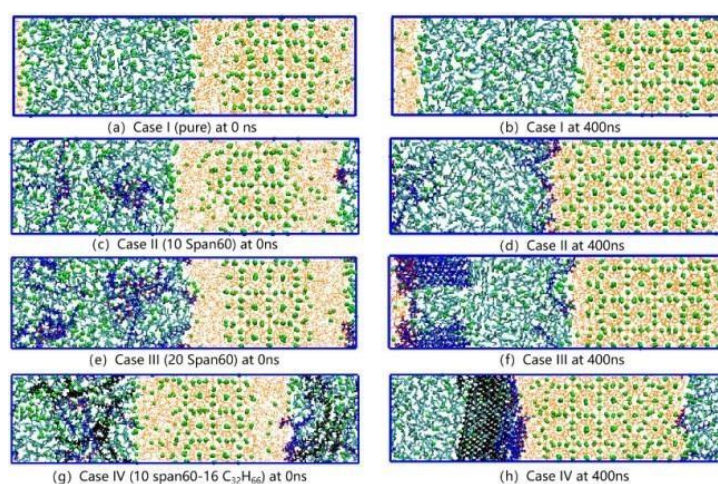


Figure 1. Four cases at critical simulation times (orange, H_2O ; green, CH_4 ; cyan, C_7H_{16} ; blue, Span60; red, the oxygen of Span60; black, $C_{32}H_{66}$).

Session 2: Flow assurance and flow modeling

Chair: Ana Cameirao, Rigoberto Morales, Michele Ciulla

Novel method and device to detect gas hydrates formation likelihood inside a pipeline

Simone Arca¹, Emilio D'Alessandro¹, Matteo Bajocco¹, Francesco Morodei¹, Claudio Passucci²,
Alfiero Leoni³, Gianluca Barile³, Vincenzo Stornelli³,

¹ *DG Impianti Industriali S.p.A. Piazza Ettore Troilo, 8 – 65125 Pescara, Italy*

² *Eni Natural Resource - MAINT Mechanical Inspection, Via Emilia 1 S. D. Milanese, Italy*

³ *University of L'Aquila, DIIE, P.le Pontieri 1 67100 L'Aquila, Italy*

Hydrated formation inside a pipeline represent one of the most concerns related to flow assurance in a pipeline. A novel miniaturized multiparametric sensor has been develop to measure critical parameters directly inside a pipeline during production. The device developed has very small dimensions, 45x35x24mm, and allow for measuring pressure ranging from 1 to 200 bar, temperature ranging from -20 to 80°C 3 axial acceleration ranging from 1g to 16g, 3 axial rotation ranging from 1 to 2000 dps, a sampling frequency setttable from 1 to 200 hz and a battery ranging from 48 to 72h. The device have been realized built in a special epoxy resin oil-proof, gas-proof, and water-proof and capable to withstand the chemical harsh environment typical of a pipeline. It is also equipped with an optional floating shell capable to make the same floatable and thus free flowing inside the oil stream. The devices recharge and communication is completely wireless in order to obtain an intrinsic protection of the electronics from the environment. The user manages the system and collects useful data at a high level by means of a dedicated software application. Thanks to the application of such device it is possible to record a pressure and temperature profile along the entire pipeline. By matching these data with accelerations records inside the pipeline it is possible to establish where the formation of gas hydrates is more likelihood. Moreover is also possible to establish if a deposit is probably forming or if a gas hydrate remediation action is effective or if it went successful or not. We report a real data referring a device mission carried out in a ENI Gulf of Mexico Field.

Sustainability Benefits of Switching from Thermodynamic Hydrate Inhibitors to Anti-Agglomerant Low Dosage Hydrate Inhibitors

Jeremy Bartels,¹ Regan Jones,¹ Vic Keasler,¹ Saugata Gon,¹ Chris Popeney,¹ Corbin Metoyer,¹ Rebecca Lucente-Schultz¹

¹ *ChampionX, Sugar Land, Texas, USA, corresponding author email :*

jeremy.bartels@championx.com

Anti-Agglomerant Low Dosage Hydrate Inhibitors (AA-LDHIs) are commonly used to prevent flowline blockages from natural gas hydrate formation on offshore production platforms for both continuous production and shut-in/re-start scenarios. They are predominantly used in the Gulf of Mexico (GoM) and gaining interest in regions with more stringent environmental regulations (UK, Norway, West Africa, Canada, Asia-Pacific, Australia), which currently only utilize thermodynamic inhibitors (THIs) such as methanol and ethylene glycol for hydrate control.

The use of THIs for hydrate mitigation is effective but requires much higher volumes of chemical – often 30-70 vol% based on the brine phase vs 0.5 – 1.5 vol% for AA-LDHIs. In higher water cut scenarios, impractical levels of THI delivery is quickly reached, making it impossible to further produce the well due to the sheer volume of THI required to prevent hydrates. Due to these limitations of THIs, the development of new AA-LDHI chemistries with improved environmental properties presents a great advantage to the oil and gas industry.

While swapping from THIs to AA-LDHIs has many practical benefits, there are also substantial sustainability benefits – particularly based on volume usage and carbon footprint. While methanol and ethylene glycol have a lower carbon footprint per kg of material than AA-LDHIs to manufacture, the volume requirement for THI-based hydrate mitigation leads to an order of magnitude higher CO₂ emission vs that of AA-LDHI. Switching to an AA-LDHI hydrate mitigation program from a THI program not only results in an overall carbon footprint reduction based on the amount of product manufactured, but there are additional emission reductions associated with the transportation/logistics to site, crane lifts onto a platform and/or pump usage to deliver the product. Background carbon footprint values, example scenarios, and well lifetime calculations will be presented.

Analysis parameters for evaluating gas hydrate kinetic inhibitor by pressurized microcalorimetry

Fagner Cabral¹, Kelly Silveira², Cristina Andrade³, Elizabete Lucas^{1,4}

¹Federal University of Rio de Janeiro, Institute of Macromolecules, Rio de Janeiro, Brazil,
fagnerlacabral@gmail.com, elucas@ima.ufrj.br

²State University of Rio de Janeiro, Polytechnic Institute, Rio de Janeiro, Brazil,
kelly.dasilveira@iprj.uerj.br

³Federal University of Rio de Janeiro, Chemistry Institute, Rio de Janeiro, Brazil,
cristaoandrade@gmail.com

⁴Federal University of Rio de Janeiro, COPPE/PEMM, Rio de Janeiro, Brazil,
elucas@metalmat.ufrj.br

Some parameters used to evaluate polymeric gas hydrate inhibitors using pressurized microcalorimetry equipment (μ -HPDSC) may not always correlate with conventional performance tests, which can influence outcome measurements. This study used the commercial inhibitor LUVICAP® 55W to investigate the effects of several parameters during the analysis: cooling and heating rates, isothermal analysis temperature, inhibition time and pressure. Using the generated data, it was established a mathematical prediction model to determine the effectiveness of the polymeric inhibitor (Figure 1). The temperature of gas hydrate formation was evaluated with heating and cooling rates varying between $0.1 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ and $1.0 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$. Isothermal analyses compared the inhibition time of the polymer against ultrapure water between $-14 \text{ }^\circ\text{C}$ and $-8 \text{ }^\circ\text{C}$, under pressures of 100 and 200 bar. Results showed no statistically significant impact of cooling/heating rates or pressure on the hydrate formation temperature. However, during the isothermal analysis, the hydrate dissociation temperature increased by $4 \text{ }^\circ\text{C}$ and the gas hydrate formation time decreased at higher working pressures. Among tested mathematical models, a second-order polynomial nonlinear regression was suitable for predicting the effectiveness inhibition (%) of the polymeric additive at different temperatures (Figure 2). Also, it was observed a curvilinear trend towards infinity with an increase or decrease in the isothermal analysis temperature as it reaches the threshold temperature values for the formation of gas hydrates. This study establishes that a temperature of $-10 \text{ }^\circ\text{C}$ is ideal for the performance analysis of the LUVICAP® 55W inhibitor using μ -HPDSC, regardless of cooling or heating rate and pressure employed in this investigation.

Acknowledgement: This study was funded by FAPERJ (E-26/200.974/2021), CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico – 305.565/2022-2), and ANP (Brazil's National Oil, Natural Gas and Biofuels Agency) through the R&D levy regulation.

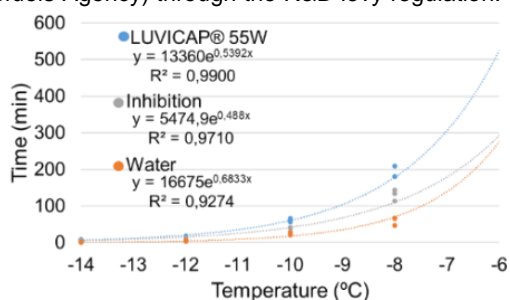


Figure 1: Gas hydrate formation trend curves as a function of temperature increase at 100 bar

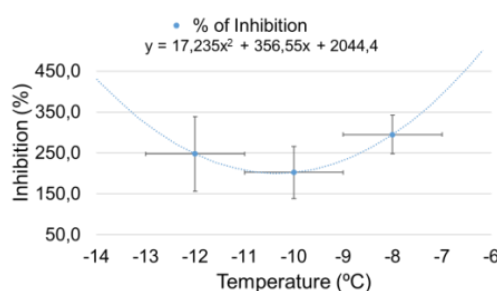


Figure 2: Curve of % inhibition of gas hydrate formation as a function of working temperature at 100 bar

A Transient Model to Predict Hydrate Slurry Flow in Horizontal Undulating-Pass in Gas/Oil/Water-Dominated systems

Haoqi /Chen¹, Bohui /Shi^{1,2*}, Shangfei /Song¹, Enqi /Guo¹, Lihao /liu¹, Jing /Gong¹

¹ National Engineering Research Center of Oil and Gas Pipeline Transportation Safety/ MOE Key Laboratory of Petroleum Engineering/ Beijing Key Laboratory of Urban Oil and Gas Distribution Technology/ China's Oil and Gas Exploration and Development Company (CNODC), Beijing, haoqi@foxmail.com

² College of Carbon Neutral Energy, China university of Petroleum-Beijing, Beijing, bh.sh@cup.edu.cn

* Corresponding author(s): Bohui Shi (bh.shi@cup.edu.cn)

In the operation conditions of deep-sea, hydrate could cause blockages in pipelines and subsea facilities. A transient simulation tool for the hydrate slurry flow is crucial for hydrate flow assurance in the petroleum industry. In this work, a new transient model is proposed for hydrate slurry flow in gas-dominated, oil-dominated and water-dominated flowlines. A two-fluid model and a temperature equation are used to describe the gas-slurry two-phase flow. For the modeling of particulate phase flow in oil-dominated system, number density conservation equation and diameter conservation equation of the hydrate particles are established by Eulerian approach, a momentum conservation equation is established by Lagrangian approach. Furthermore, combining with the hydrate formation model, the transient gas hydrate slurry flow in oil-dominated flowlines can be numerically simulated. For the gas/water-dominated, the model assumes that hydrates are uniformly dispersed in the liquid phase and flow in the form of hydrate slurry. Especially, the Euler-Euler method is employed to observe the flow characteristics of both the fluid and hydrate phase, determining the migration process of hydrates within the pipeline. The impact of the exothermic phase change process of hydrates on the flow variables is considered. To verify the rationality of the model, the transient behavior of the gas-hydrate slurry multiphase flow upon reduced gas well production. These results (Figure 1) are of great practical value to give a deeper understanding of hydrate slurry multiphase flow, and contribute to better hydrate management in the petroleum industry by using hydrate slurry flow technology.

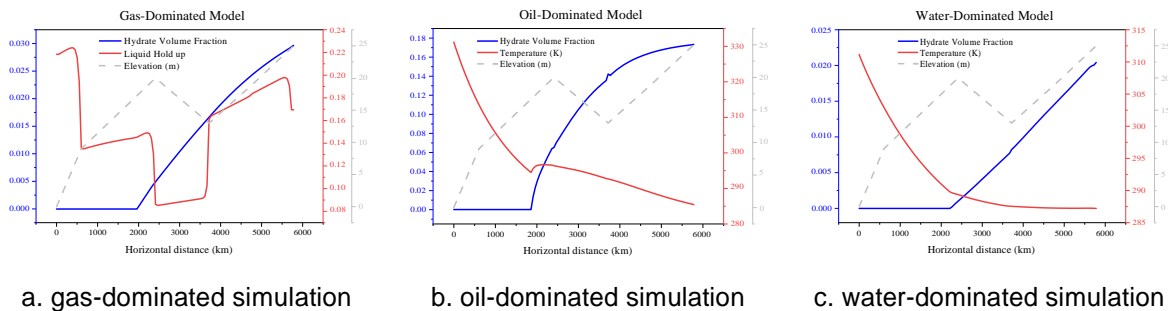


Figure 1. Steady state simulation results of the pipeline in different systems

Experimental investigation of gas hydrate formation in crude oil and high salinity systems

Luiz De Vasconcelos¹, Celina Kakitani¹, Amadeu K. Sum²,
Moises A. Marcelino Neto¹, Rigoberto E. M. Morales¹

¹*Multiphase Flow Research Center, NUEM, Federal University of Technology of Paraná, Curitiba
80230-901 Paraná, Brazil, luizvasconcelos@alunos.utfpr.edu.br, ckakitani@gmail.com,
mneto@utfpr.edu.br, rmorales@utfpr.edu.br*

²*Phases to Flow Laboratory, Chemical and Biological Engineering Department, Colorado School of
Mines, Golden, Colorado, USA, asum@mines.edu*

Gas hydrate formation is a significant challenge in the oil and gas production due to its potential to cause pipeline blockages, resulting in revenue losses and safety hazards. Testing with crude oil provides the advantage of conducting analyses under conditions similar to those encountered in field operations, including compositions and interactions. This allows for a more accurate observation of results that closely mimic field conditions compared to using a model oil. One potential advantage of high salinity systems is the reduced need for chemical additives, as salts, which are already present in production water and are abundant, can assist in producing a transportable hydrate slurry with minimal or no chemical injection required.

This study experimentally characterizes hydrate formation in high-salinity systems and their impact on hydrate transportability, considering multiphase sheared conditions, quantified in terms of hydrate agglomeration, wall deposition, and bedding as investigated in a rock-flow cell. Experimental measurements were done for pressures of up to 80 bar from a three-phase system (water, natural gas, crude oil), with collection of pressure, temperature, and video/images. Hydrate formation was assessed for various conditions, including water cuts (10-50%), liquid loading (20-60%), subcooling (5-15°C), and salt concentration (up to 16 wt%). In fresh water systems, higher water cuts showed a hydrate bedding due to the limited shear, whereas for lower water cuts a dispersed systems with wall deposition was observed. Salt concentration and water cut had a direct impact on hydrate formation, highlighting their influential role in shaping the morphological profiles observed. Two major effects were observed independently: hydrate risk was found to increase with water cut, producing large aggregation and high adhesion wall deposits, whereas hydrate dispersion increased with salinity favoring the formation of hydrate slurry. No specific trend was observed regarding subcooling. This research emphasizes the importance of effective management strategies, considering factors like subcooling, water cuts and salinity, for safer oil and gas production operations.

Mechanistic Model of Hydrate Deposition Processes in Horizontal Oil-Dominated Flows

Enqi /Guo¹, Bohui /Shi^{1,2*}, Shangfei /Song¹, Haoqi /Chen¹, Lihao /Liu¹, Jing /Gong¹
¹ National Engineering Research Center of Oil and Gas Pipeline Transportation Safety/ MOE Key Laboratory of Petroleum Engineering/ Beijing Key Laboratory of Urban Oil and Gas Distribution Technology/ China's Oil and Gas Exploration and Development Company (CNODC), Beijing, enqig@foxmail.com

² College of Carbon Neutral Energy, China university of Petroleum-Beijing, Beijing, bh.sh@cup.edu.cn

* Corresponding author(s): Bohui Shi (bh.shi@cup.edu.cn)

Hydrate formation and blockage are the main problems of flow assurance in deepwater multi-phase pipeline. Although existing research have been proposed many conceptual understandings, there are still few mathematical models to quantify this process. In this paper, a quantitative prediction model for the mechanistic process of hydrate deposition in horizontal pipelines within oil-dominated systems is established by coupling the boundary layer theory, pipe flow shear model, roughness of pipe wall and particle packing structure. The Sauter mean droplet diameter is used as the initial particle size of hydrate growth, and the hydrate shell thickness and particle size change are calculated by the hydrate formation model. After considering the adhesion between particles, the size of hydrate aggregates is given by using the hydrate aggregation model. Then, through the force analysis of hydrate aggregates in the flow system, such as drag force, lift force, etc., the model of critical deposition velocity of hydrate particles is established. And then, the equilibrium analysis of force and moment such as van der Waals force and friction force is carried out on the aggregates falling into the boundary layer, and the condition of particle removal without liquid bridge is proposed. Finally, based on the particle accumulation mode, the thickness of the hydrate deposition layer along the pipeline is given by the iterative calculation model, and the effective inner radius of the pipeline is used to characterize the hydrate blockage state (Figure 1). This study contributes to a better understanding of the key problems in the process of hydrate deposition in deepwater gathering systems. By accurately predicting the location and time interval of hydrate deposition and quantitatively predicting hydrate deposition within the horizontal pipeline, it provides theoretical supports for the development of hydrate management strategies in oil and gas pipelines.

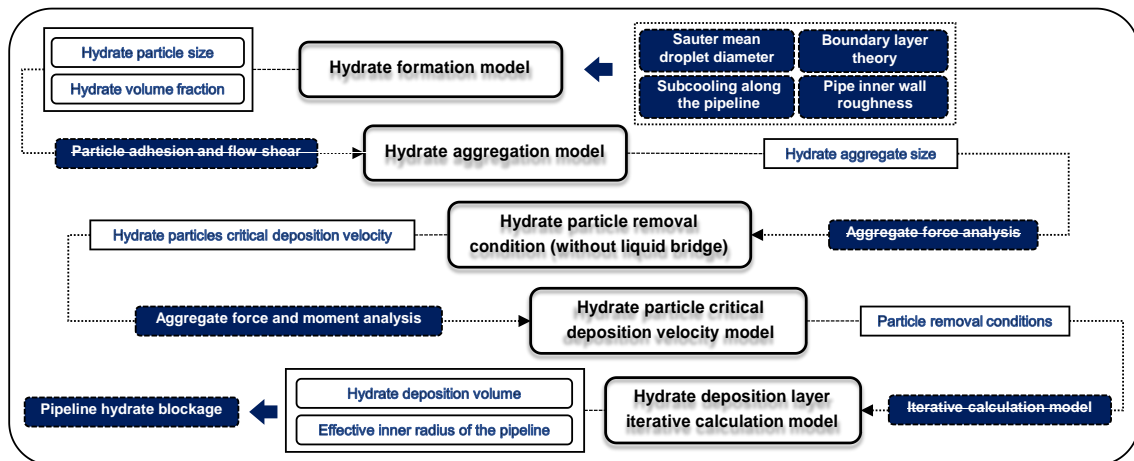


Figure 1. Hydrate deposition process flow chart

Oil/Water Partitioning of Environmentally Improved Anti-Agglomerant Low Dosage Hydrate Inhibitor

Regan Jones¹, Jeremy Bartels¹, Corbin Metoyer¹, Rebecca Lucente-Schultz¹

¹ *ChampionX, Sugar Land, TX, USA, corresponding author email: regan.jones@championx.com*

Anti-agglomerant low dosage hydrate inhibitors (AA-LDHIs) are commonly used to prevent flowline blockages due to natural gas hydrate formation on offshore production platforms in the Gulf of Mexico. They prevent hydrate plugs by dispersing hydrates into a fine slurry that can be safely pumped through the flowline. They are effective for both continuous production and shut-in/re-start scenarios. While AA-LDHIs are broadly applied in the Gulf of Mexico, their use has been extremely limited in regions with more stringent environmental regulations (North Sea, West Africa, Canada, Asia-Pacific, Australia).

Usage outside the Gulf of Mexico is restricted because traditional AA-LDHI products do not satisfy the toxicity, biodegradation, and bioaccumulation regulations in other areas. In these regions, producers rely on thermodynamic hydrate inhibitor (THI) solvents such as methanol and ethylene glycol to prevent gas hydrates. This strategy is effective but requires much higher volumes of chemical. In high water cut scenarios, it may be impractical or, in some cases impossible, to produce the well due to the amount of THI required for hydrate inhibition. Due to these limitations of THIs, the development of new AA-LDHI chemistries with improved environmental properties presents a significant advantage to the oil and gas industry.

An AA-LDHI chemistry has been developed that meets the environmental requirements for application in the North Sea. This product was granted a Cefas banding of Silver (with a substitution warning) and classified Y1 Yellow by the Norway Environmental Agency. Recently, the new AA-LDHI underwent a successful topsides trial in the North Sea. The AA-LDHI did not impact water quality or phase separation in the trial even when the chemistry was injected at >3x the required dose rate for hydrate control. As part of the trial, the oil/water partitioning of the novel AA-LDHI was also studied since it is more hydrophilic (lower Log P_{ow}) than traditional AA-LDHIs. The partitioning study showed that despite the relatively more hydrophilic nature of the active, the product still shows heavy predominance in the oil phase. This finding is pertinent to the validation and adoption of the new environmentally improved technology as the product is introduced into the market.

Study on the hydrate dissociation in the high-pressure flow loop

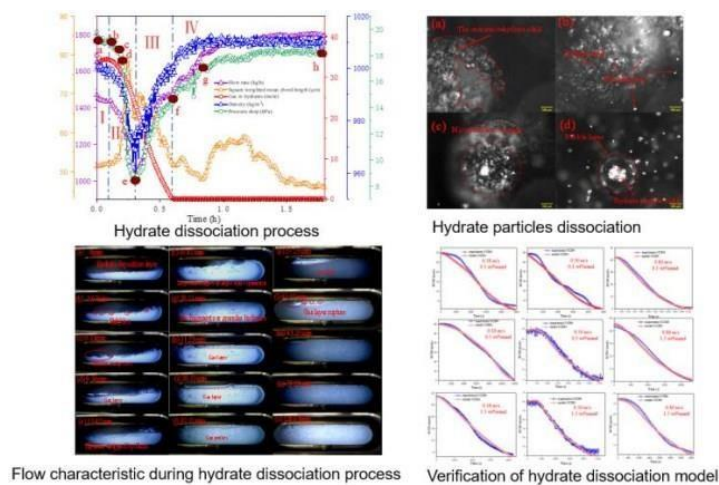
Lihao /liu¹, Shangfei /Song^{1*}, Bohui /Shi¹, Peiyong/zhang², Haoqi /Chen¹, Enqi /Guo¹, Yumo/Zhu¹, Jing /Gong¹

¹ National Engineering Research Center of Oil and Gas Pipeline Transportation Safety/ MOE Key Laboratory of Petroleum Engineering/ Beijing Key Laboratory of Urban Oil and Gas Distribution Technology/ China's Oil and Gas Exploration and Development Company (CNODC), Beijing, liulihao72@163.com

² Research Institute of Natural Gas Technology, Petrochina Southwest Oil & Gasfield Company, Chengdu, Sichuan, China

* Corresponding author(s): Shangfei Song (song.sf@cup.edu.cn)

During the hydrate solid fluidization exploitation, due to changes in external pressure and temperature, gas hydrates gradually decompose within the pipeline, causing the internal fluid to transition from a solid-liquid two-phase flow to a gas-liquid-solid three-phase flow. Currently, the majority of research on the dissociation mechanism of gas hydrate reservoir exploitation focuses on porous media, sediment systems, or stirred tank systems. However, there is a dearth of research examining the dissociation of natural gas hydrates under flowing conditions within different systems. Therefore, the hydrates slurry dissociation mechanism and flow characteristics are studied by horizontal high-pressure flow loop experiments. Results indicated that the hydrate and slurry dissociation process in the flow loop is divided into four stages. The alteration in flow characteristics is attributed to two main factors. Firstly, the dissociation of gas hydrates reduces the viscosity of the fluid. Secondly, the release of gas molecules from the hydrates leads to saturation in the solution, resulting in the formation of numerous micro- and nano-bubbles. These bubbles will adhere to the surface of hydrate sand aggregates, change the frictional resistance between solid and liquid, and form gas-liquid two-phase mixed flow in the near wall region. This flow state reduces the fluid density near the wall boundary layer, thereby altering the overall flow characteristics of the fluid. Specifically, some solid-liquid interfaces transform into slip gas-liquid interfaces without shear stress, effectively reducing the drag force between the solid-liquid interfaces. At the same time, convergence, fusion, and other phenomena may occur between bubbles, forming complex structures such as airbags, chambers, or gas layers, changing the flow pattern of the fluid. Then, based on the micro-scale dissociation mechanism of methane gas hydrates and the three-step process of hydrate dissociation, which includes the desorption of gas molecules from the guest cages, the collapse of the guest cages and basic cages, and the diffusion of gas molecules into the bulk phase, a new model is established to describe hydrate dissociation that considers both intrinsic kinetics and mass transfer within the flowing system.



Direct-Imaging System Using Electrical Impedance for Hydrates Monitoring in Rock-Flow Cell

Jean P. N. /Longo¹, Natan S. /Reginaldo¹, Everton /Trento¹, Moisés A. /Marcelino Neto¹, Rigoberto E.M. /Morales¹, Marco /da Silva², Eduardo /dos Santos¹

¹ Multiphase Flow Research Center (NUEM), Universidade Tecnológica Federal do Paraná, Curitiba, Brazil, ensantos@utfpr.edu.br

² Institute for Measurement Technology at the University of Linz

Hydrate management in the oil and gas industry is essential nowadays, especially because of the operational risk regarding safety and also the economic problem once a production stoppage may result in significant losses. To mitigate the risk of accidents, reduce financial losses and also bring a better understanding about hydrates, electrical impedance can be a strong ally in detecting the formation of these crystalline structures within pipelines.

Therefore, a new sensor geometry was designed to be applied to rock-flow cells in a way that does not disturb the flow (non-intrusive) and that allows monitoring mainly the internal walls, being capable of detecting the hydrates deposition.

Several Finite Element Method (FEM) simulations were performed to reach such geometry and to understand the electric field behavior. With this method, it is possible to comprehend the sensor's response regarding the internal material properties once it models how the electric field behaves within different mediums. The simulations show that the proposed geometry, combined with electrical impedance measurements, can be effective in detecting changes in the physical state of the medium, and due to the arrangement of the electrodes, it will be possible to perform direct-imaging from rock-flow cell inner walls using electronics that are being developed especially for this purpose. With that, it will be possible to multiplex the channels, and we will be able to compare the results with commercial equipment. Finally, in the future, it will also be possible to carry out real experiments using real fluids from the oil exploration process. Figure 1 depicts an overview of the entire system.

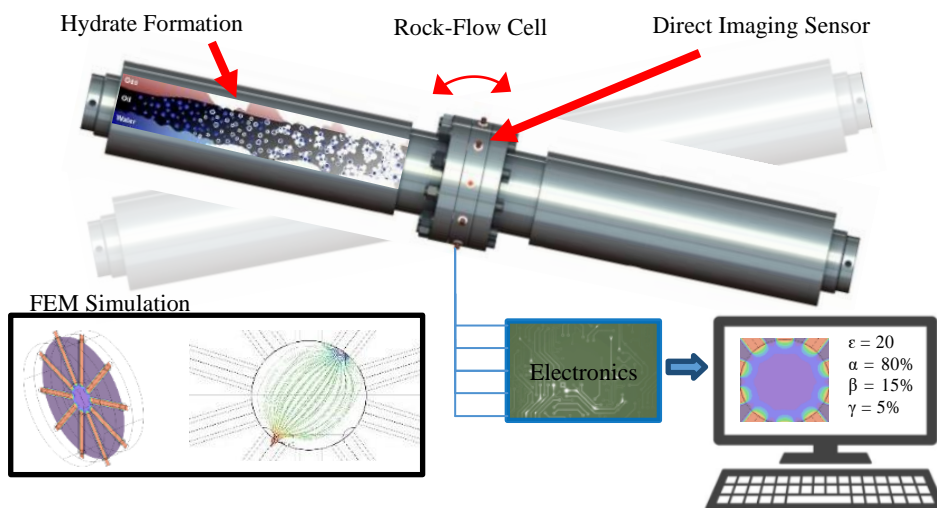


Figure 1- Rock-flow cell with the sensor in the middle, FEM simulations of electric potential and electric field behavior, dedicated electronics and the control system with data acquisition

Influence of hydrate-like particles in stratified and slug multiphase flow

Vitor O. O. Machado¹, Stella Cavalli¹, Paul A. D. Maldonado¹, Gianluca Lavallo², Eduardo N. dos Santos¹, Moisés A. Marcelino Neto¹, Ana Cameirão², Amadeu K. Sum³, Rigoberto E. M. Morales¹

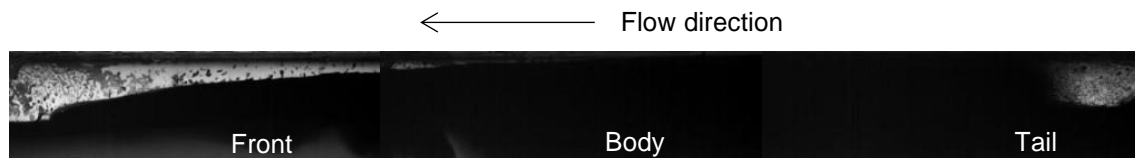
¹Multiphase Flow Research Center (NUEM), Federal University of Technology – Paraná (UTFPR), Curitiba, 81280-340, Brazil

²Mines Saint-Etienne, Univ Lyon, CNRS, UMR 5307 LGF, Centre SPIN, Saint-Etienne, France

³Phases to Flow Laboratory, Colorado School of Mines, Golden, Colorado 80401, USA

Gas hydrates are solid substances formed at high pressures and low temperatures that pose a significant threat to oil and gas operation given their potential to agglomerate and to cause pipe blockage. There are two main strategies to deal with hydrates: the traditional hydrate avoidance approach, which consists of preventing the conditions that lead to hydrate formation; and the focus of the present work, hydrate management, which allows hydrates to form while using anti-agglomerants to prevent their agglomeration. In such a scenario, the formed hydrate particles are carried within the liquid phase, resulting in a hydrate slurry flow. Despite the importance of this topic, there is limited literature available on the impact of these particles on key flow parameters, including pressure drop, liquid holdup, and overall flow topology. The aim of this study is to address these gaps, specifically focusing on the stratified and slug flow patterns. Experiments using air and water as working fluids were performed, with model polyethylene particles with a density close to that of hydrates, in a 50-mm inner diameter, 34-m long flow loop. Four different particle concentrations were investigated: 0%, 5%, 10%, and 20% v/v in the liquid phase. In stratified flow, the pressure drop increased by increasing the particle concentration while the liquid level experienced minor variations. At low flow velocities, particularly at high particle concentrations (10% and 20% v/v), poor particle transportability resulted in partial blockage of the pipeline. At low gas velocities, the blockage arose as a layer of non-moving solids. However, at higher gas velocities, this layer became unstable, forming structures similar to slugs, shown in Figure 1, even under stratified flow conditions.

Figure 1 – Slug like structure that arose from poor particle transportability



In both scenarios, the pressure loss was much higher than that of regular stratified flow. On the other hand, the changes in the pressure drop were less drastic for slug flow. For all particle concentrations, a slight increase in pressure drop was observed at low liquid superficial velocities. However, at high liquid superficial velocities, which led to more dispersed particles, the pressure loss showed minor variations. The velocity of elongated bubbles decreased when particles were introduced. This was attributed to a layer of particles forming around the bubbles, thus causing a virtual mass effect. The presence of particles also led to rearrangements of the slug unit cell, with the lengths of both the elongated bubble and the liquid slug showing variations within 30% when compared to a flow without particles.

Transportability of a hydrate slurry in the presence of wax

Luiz Henrique Meneghel Lino¹, Gianluca Lavallo¹, Eric Serris¹, Jean Michel Herri¹, Ana Cameirao¹,
Nicolas Lesage², Annie Fidel Dufour²

¹ Univ. Lyon, CNRS, UMR 5307 LGF, Centre SPIN, F-42023 Saint-Etienne, France

² Total Energies, Pau, France

One of the main concerns of flow assurance is to deal with the solid transportation within the production facilities, especially in offshore oil and gas production. Among the solids with possible occurrence, gas hydrates and wax are recognized as those with potential to cause major blockage of the pipeline. This work aims to experimentally investigate the transportability of a hydrate slurry in the presence of wax by means of a high-pressure and low-temperature flow loop. In particular, this research is focusing on wax/ hydrate interaction and the role of wax on the hydrate formation and on the plugging/ transport mechanism. For this, wax-free experiments were conducted and compared with experiments in the presence of wax. In addition, different liquid flow rates (200 and 400 L/h) and water-cut (10 and 30 %) were tested to assess the impact of the hydrodynamic and the quantity of hydrate in the blockages mechanisms.

The flow loop comprises several probes such as acoustic emission and permittivity, as well as a high-speed camera and microscope. The working fluids are a model oil (Kerdane oil and 2 wt % of synthetic wax), saline water (30 g/L) and synthetic natural gas. The different probes installed at the flow loop allows the identification of the flow pattern before and after hydrate formation, as well as the plugging mechanism.

At lower water cut, a low plugging risk is observed both with and without wax, with hydrates agglomerating and depositing shortly after the nucleation onset. The main difference caused by the presence of wax is a significative reduction on the hydrate fraction for the wax-containing system, as can be seen in Figure 1 (a). At higher cut (30 % of water) hydrates agglomerate and accumulate in preferential portions of the loop a few minutes after the onset. This accumulation occurs both with and without wax and creates a high local hydrate fraction, leading to plug the pipe shortly before the hydrate onset. Also, at 30 % water cut, the presence of wax does not impact significantly the water conversion (Figure 1 (b)).

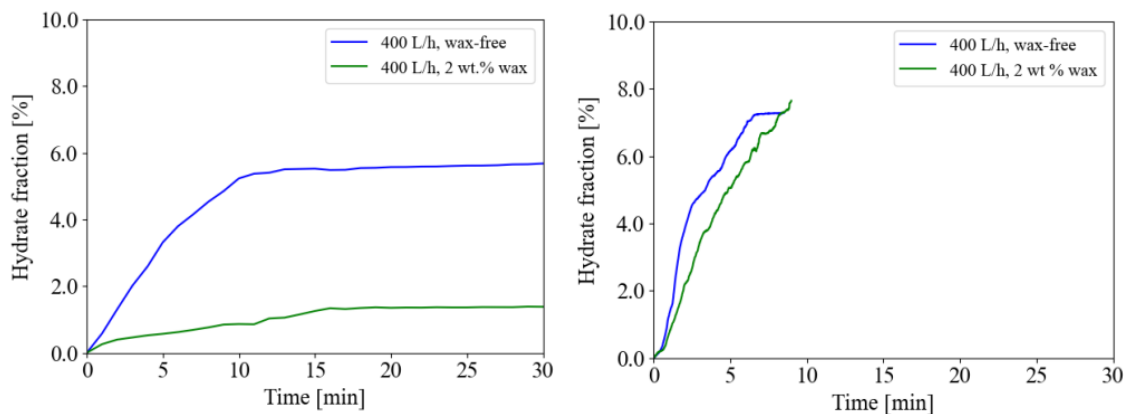


Figure 1 - Calculated hydrate fraction at for 400 L/h for wax-free (blue line) and wax-containing (green line) for (a) 10 % water cut and (b) 30 % water cut.

Gas-Liquid Flow Experiments and Modeling in a Novel Rocking and Rolling Flow Loop

Madina Naukanova^{1,2}, Gianluca Lavallo², Jerome Douzet², Ana Cameirao², Jean-Michel Herri².

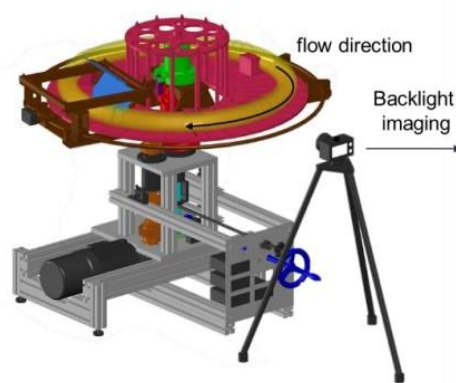
¹ IFP Energies Nouvelles, 69360 Solaize, France

² Mines Saint-Étienne, Univ Lyon, CNRS, UMR 5307 LGF, Centre SPIN, F - 42023 Saint-Étienne, France

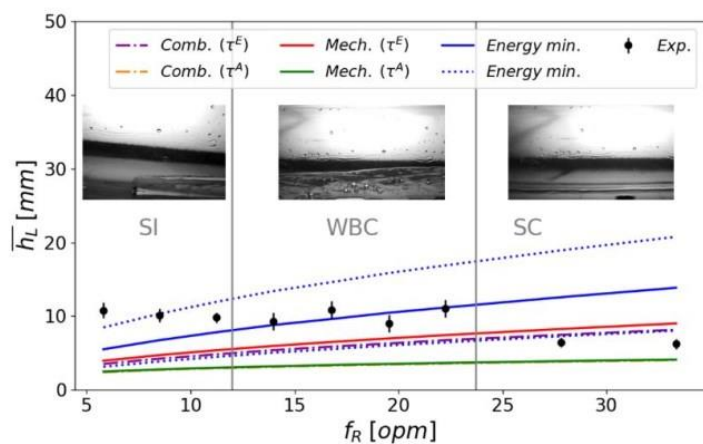
Gas hydrate formation in oil production pipelines can lead to flow blockages, posing significant financial and safety risks. One proposed strategy to mitigate this issue involves the use of anti-agglomerants to reduce particle adhesion and facilitate flow alongside hydrates. However, the successful implementation of such a strategy requires a thorough understanding of the interplay between hydrate formation and multiphase flow characteristics, i.e. pressure drop, liquid height and flow regime. Besides, monitoring the performance of potential anti-agglomerants before industrialization is crucial. These aspects require efficient flow testing facilities capable of replicating industrial flow conditions. To address this need, we introduce the Rocking and Rolling Ring Flow Loop (3RFL), a novel experimental device that is both cost-effective and time-efficient.

In this study, we conduct air-water flow experiments using the 3RFL apparatus under atmospheric pressure and temperature conditions. However, our ultimate objective is to develop an experimental setup capable of accurately capturing pressurized reactive multiphase flow dynamics relevant to the flow assurance domain. The 3RFL is displayed in Fig. 1 can generate various flow regimes by adjusting key control parameters such as rocking angle, rocking rate, and liquid volume fraction, all without the need for a pump. Through our experiments, we identify three distinct flow regimes and examine the influence of control parameters on their emergence and transitions.

We find that flow regime transitions are primarily influenced by the competition between gravitational and centrifugal forces, which arise from the curvature of the tube. Furthermore, by comparing three modeling strategies—mechanistic modeling, total energy minimization, and a combined approach—we determine that the total energy minimization model provides the closest approximation to experimental liquid height.



LxWxH = 1.2 x 1.2 x 1.2 m³
 Diameter of the tube: 69.85 mm
 Total Volume: ~ 10 L



SI - Smooth Interrupted, WBC - Wavy-Bubbly Continuous, SC - Smooth Continuous

Figure 1. Left: Sketch of the 3RFL. Right: Comparison between experimental and predicted liquid height results.

Deposition and agglomeration characteristics of gas hydrates in natural gas pipelines by using chemical additives

Seongah/Park¹, Jeong-Hoon/Sa²

¹ *Department of Chemical Engineering, Dong-A University, Busan, South Korea,
1830273@donga.ac.kr*

² *Department of Chemical Engineering, Dong-A University, Busan, South Korea, jhsa@dau.ac.kr*

In the pipelines connecting from the wellhead to production facilities in oil/gas production systems, gas hydrates can form when exposed to low temperatures and high pressures as long as the sufficient amount of moisture is present inside. When hydrates form under such conditions, the pipe interior becomes narrow, causing a large pressure drop. If they are not properly treated, pipeline blockages would potentially occur. Therefore, it is necessary to proactively identify risk factors caused by hydrate formation that may occur when transporting natural gas and oil through pipelines. A proper management of hydrate formation risks is needed in flow assurance. In this study, we used a synthetic model natural gas (75% CH₄/25% C₂H₆), which forms structure II hydrate, and a mixture of water and mineral oil to test hydrate formation scenarios under multiphase flow conditions. Experiments were conducted by adjusting the liquid loading, water cut, and the rocking angle/speed to simulate different flow patterns. Experimental temperature was set to 4 °C, simulating subsea environment, and phase equilibrium conditions of natural gas hydrates were calculated by using CSMGem. The effect of span 80, a commercially available anti-agglomerant (AA), on hydrate deposition and agglomeration characteristics was studied. In addition, amino acids as environmentally friendly kinetic hydrate inhibitors (KHIs) with different hydrophilic-hydrophobic balances were used to investigate their synergistic effect with the use of AAs. The synergistic or uncooperative effects of AAs-KHIs were investigated by morphological observation of hydrate deposition and agglomeration behaviors. Based on the experimental results, the mapping the level of risk depending on the test conditions by using the 'Hydrate Flow Risk Index'. Our experimental results would simulate further flow assurance studies on shut-in and restart cases that are often encountered in actual oil and gas pipelines. Our findings would contribute to derive the efficient strategies for securing flow stability under multiphase flow conditions encountered in oil and gas production pipelines.

Efficient Gas Hydrate Characterization for Flow Assurance: A Focus on Thermodynamic and Kinetic Analysis

Ernesto Petteruti, Marco Buccolini, Andrea Quaranta, CHIMEC Spa
Simone Arca, Emilio D'Alessandro, RDPower

Gas hydrates characterization is crucial in flow assurance for the safe and efficient transportation of hydrocarbons through pipelines. This work highlights the usage of a versatile apparatus for both thermodynamic and kinetic characterization of gas hydrates, essential in the oil and gas industry. The equipment operates from 0 to 200 bar and -20 to +40°C, enabling a comprehensive understanding of hydrate behavior under diverse conditions. It also offers precise control during experiments with a torque range of 0 to 20 N*cm and RPM range of 0 to 1500. Utilizing this apparatus, we have developed efficient methodologies for gas hydrate characterization. Kinetic studies are rapid and reproducible, providing reliable data for industrial applications. Thermodynamic characterizations closely align with literature data, ensuring the equipment's accuracy and reliability. These methodologies are significant for flow assurance, offering essential information to prevent pipeline blockages. The apparatus excels in analyzing various Hydrate Inhibitors, focusing on Low Dosage Hydrate Inhibitors (LDHIs), encompassing both Kinetic Hydrate Inhibitors (KHIs) and Anti-Agglomerants (AAs), as well as Thermodynamic Inhibitors (TDIs), thereby providing critical insights into diverse hydrate management strategies. Our techniques offer a comprehensive analysis of inhibitor performance, aiding the safe transport of hydrocarbons and mitigating hydrate formation risks. In conclusion, this research utilizes a versatile apparatus to enhance our understanding of gas hydrates and flow assurance. The developed methodologies are efficient, reliable, and provide in-depth insight into hydrate behavior and inhibitor performance, contributing significantly to hydrate research and hydrocarbon transportation.

Understanding Methane Hydrate Adhesion on Surfaces: A Preliminary Investigation

Serena Pilato¹, Michele Ciulla¹, Gabriella Siani¹, Samanta Moffa¹, Nadia Barbacane¹, Rafal Damian Wolicki¹, Antonella Fontana¹, Pietro Di Profio^{1,*}

¹ Department of Pharmacy, University "G. d'Annunzio" of Chieti-Pescara, via dei Vestini 31, 66010 Chieti, Italy.

*Corresponding author: P. Di Profio (pietro.diprofio@unich.it)

The safe and efficient transportation of natural gas through pipelines is critical for modern energy infrastructures. However, a significant challenge is posed by clathrate hydrates, ice-like crystalline structures that can form under specific temperature and pressure conditions. The formation of hydrates within pipelines presents a major threat, potentially leading to flow blockage and the consequent equipment damage and economic losses. Furthermore, the release of pressurized gas due to hydrate blockages can create fire and explosion hazards, posing serious risks to personnel and the environment [1]. To avoid hydrate formation, several kinds of additives have been used in these years: thermodynamic inhibitors such as methanol and glycols, and low-dosage hydrate inhibitors [2]. The latter may be divided into kinetic inhibitors and anti-agglomerants. Despite the adoption of chemical inhibitors is widely recognized, it includes risks related to the toxicity, corrosivity, and environmental problems due to the chemicals itself. Alongside this strategy, research has also focused on the ability of different materials to block or at least reduce the formation of hydrates on the walls of pipelines, thus allowing to reduce the concentration of chemical inhibitors. In this context, hydrate agglomeration and deposition are the two main processes that form hydrate plugging in deep-water oil and gas pipelines. An important case of hydrate deposition is when hydrate grows directly on the pipe wall, which has been not often studied in the literature [3]. It is crucial to understand the adhesion strength of the hydrate deposits to advance the management of hydrate formation and avoid plugging in pipelines.

The aim of this work was to test the adhesion/interaction properties of some materials with methane hydrates. In particular, experiments were conducted in a custom laboratory apparatus, which is basically a stainless-steel reactor with a customized samples holder on the bottom, with working pressure up to 20 MPa and with a fine control of pressure and temperature, and a CCD-coupled window for visually observing inside the reactor.

Samples of different materials, with specific geometry, were tested: copper, aluminium, brass, 304 Steel, Teflon® (PTFE polytetrafluoroethylene), Delrin® (Acetal Resin) and PVC (Polyvinyl chloride). Conductivity and pH tests were also performed to assess the presence of any ions that might be released from the samples that might affect the observed adhesion behaviour. From preliminary experiments, copper had the best behaviour, since it showed a lower adhesion of methane hydrate among the tested compounds. Finally, as an attempt to reduce the adhesion of hydrates to industrially relevant surfaces, we have evaluated the adhesion forces between model (THF) hydrates and several plastic and metal surfaces coated with graphene.

Acknowledgements: funded by the European Union - NextGenerationEU under NRRP - M4C2 - Investment 1.5 - Call for tender No. 3277 of 30.12.2022 IMU "Innovation, digitalisation and sustainability for the diffused economy in Central Italy" - Concession Degree No. 1057 of 23.06.2022 - CUP: D73C22000840006

Bibliography

- [1] Carroll J. Natural Gas Hydrates—A Guide for Engineers. MA: Gulf Professional Publishing, Elsevier Science; 2003.
[2] Di Profio, P.; Canale, V.; Marvulli, F.; Zappacosta, R.; Fontana, A.; Siani, G.; Germani, R. Chemoinformatic Design of Amphiphilic Molecules for Methane Hydrate Inhibition. *J. Chemom.* 2018, 32, doi:10.1002/cem.3008.
[3] L. Chenwei, W. Zhiyuan, T. Jinlin, Y. Ci, L. Mingzhong. Fundamental investigation of the adhesion strength between cyclopentane hydrate deposition and solid surface materials, *Chemical Engineering Science*, 217, 2020, 115524.

Experimental determination of methane diffusivity in water and brine under hydrate formation conditions

Thales H Sirino¹, Celina Kakitani¹, Luiz F. S. Vasconcelos¹, João V. M. Rocha¹, Dalton Bertoldi¹,
Rigoberto E. M. Morales¹, Moisés A. Marcelino Neto^{1,*}

¹ *Multiphase Flow Research Center, Federal University of Technology of Parana, Curitiba/PR, Brazil*

**email: mneto@utfpr.edu.br*

Hydrate formation is a threat to oil and gas production, as hydrates can agglomerate and block the pipeline. To mitigate this problem, several methods have been employed, including the injection of kinetic inhibitors to delay crystal formation. However, for the effective application of this technique, a comprehensive understanding of the entire process is necessary. The mass transfer between the gas and the different phases in the system is one of the phenomena that can delimit the hydrate formation rate. Diffusivity is one of the most important parameters that govern the mass transfer processes. Unfortunately, there is neither an equipment capable of directly measuring diffusivity nor a universally accepted theoretical approach for its determination. Yet there are properties that can be measured experimentally and correlated to the diffusivity using models. While several authors have proposed different experimental and calculation methodologies to estimate diffusivity, many of these solutions are limited by underlying assumptions and simplifications that may lead to potential errors or limit their applicability. One common approach is the use of the continuity equation in a system where diffusion is taking place, but that requires the knowledge of the species composition over time and space. Although direct composition measurement methods can be used, they are expensive and intrusive, requiring the development of simpler methodologies. Among these, the pressure decay method is the most commonly applied method for determining the diffusivity of gases in liquids. This method involves placing a gaseous and a liquid phase in contact in a PVT cell of constant volume at a given initial pressure and temperature. As the gas diffuses into the liquid phase, there is a decrease in the system pressure, which is monitored and recorded. Using the resulting pressure profile, the continuity equation can be solved so as to determine the gas concentration gradient in the liquid and estimate the diffusivity. The objective of this study is to experimentally determine the diffusivity of methane in water and brine under hydrate formation conditions using the pressure decay method. In order to minimize the simplifications required for determining mass transfer parameters, what might lead to potential inaccuracies or restrict its applicability, a numerical model that considers the dependence of the diffusivity on solute concentration and liquid phase swelling was developed. Various boundary conditions, including quasi-equilibrium, time-dependent non-equilibrium and mass balance-based conditions were assessed on the gas-liquid interface. The saturation concentration of the solute was determined through a flash calculation using the Cubic-Plus-Association equation of state (CPA). This equation of state also yielded mixture density and gas fugacity coefficient, thus enabling the use of a thermodynamic correction factor to refine diffusivity estimates. Experiments were conducted within a temperature range of 274.15 K to 283.15 K and pressures from 35 to 90 bar, with salt concentrations up to 3.5% w/w. These conditions were so chosen so that realistic hydrate formation scenarios could be simulated.

Cases where it would be difficult to detect the causes of blockage

Bahman/Tohidi^{1,2,3}

¹ Institute of GeoEnergy Engineering, Heriot-Watt University, Edinburgh

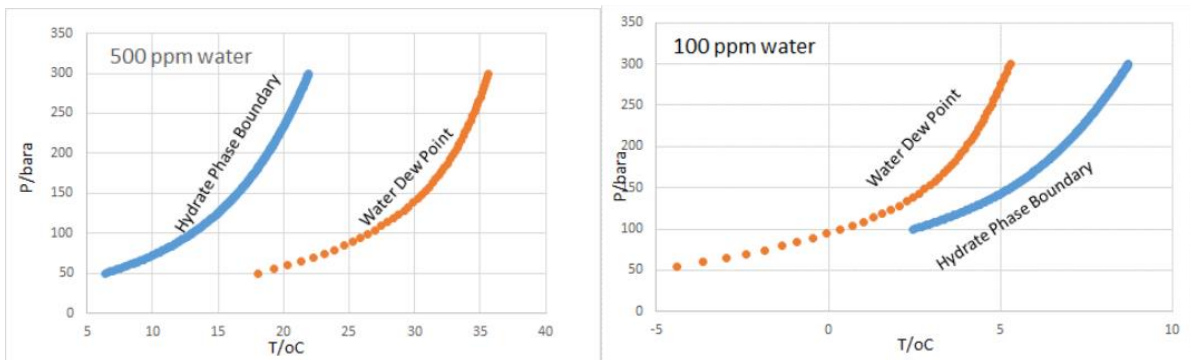
² Hydract Ltd, Heriot-Watt University Research Park, Edinburgh, bahman.tohidi@hydract.com ³ Copernicus Institute of Sustainable Development, Utrecht University, Utrecht

Gas hydrates are solid materials that can form at relatively low temperatures and elevated pressures, posing significant operational challenges when they occur within pipelines and process facilities. Detecting their presence accurately is crucial for effective mitigation. To achieve this, companies must rely on extensive engineering expertise and access to robust thermodynamic models.

In our presentations, we highlighted three case studies where identifying the root cause of blockages proved challenging due to the possibility of multiple factors contributing to the issue:

1. A buried pipeline in a winter climate experienced blockages where hydrates had converted to ice, with an additional risk of salt blockage.
2. Blockages occurred in a Cold Box, initially diagnosed as hydrates but further investigation revealed the presence of ice.
3. A subsea pipeline faced blockages during pigging operations after reducing separator pressure to match reservoir driving forces. While hydrates were initially suspected, our investigations revealed the presence of wax

Water Content & Dew/Hydrate Points, Methane-Water Systems, Prediction by HydraFLASH



Hydrocarbon-Physical Data

| IUPAC Name | Carbon No | MWt | Melting Points | IUPAC Name | Carbon No | MWt | Melting Points |
|------------|-----------|--------|----------------|---------------|-----------|--------|----------------|
| N-nonane | 9 | 128.25 | -53 | N-tridecane | 13 | 184.35 | -5 |
| N-decane | 10 | 142.28 | -30 | N-tetradecane | 14 | 198.38 | 6 |
| N-undecane | 11 | 156.3 | -26 | N-pentadecane | 15 | 212.41 | 15 |
| N-dodecane | 12 | 170.33 | -10 | N-hexadecane | 16 | 226.43 | 18 |

Session 3: Natural gas hydrate systems and climate change

Chair: Jasmina Obhoaš, Michela Giustiniani

Impact of Salts on CO₂ Hydrates and Injectivity during CO₂ Storage in Depleted Gas Fields

Mahnaz Aghajanloo¹, Sadegh M. Taghinejad¹, Denis Voskov^{1,2}, Rouhi Farajzadeh^{1,3}

¹ Delft University of Technology, Department of Geoscience and Engineering, Stevinweg 1, 2628 CN, Delft, The Netherlands, M.Aghajanloo@tudelft.nl & S.Taghinejad@studenti.polito.it
² Energy, Science and Engineering, Stanford University, D.V.Voskov@tudelft.nl
³ Shell Global Solutions International B.V., Grasweg 31, 1031 HW Amsterdam, The Netherlands), R.Farajzadeh@tudelft.nl

The utilization of subsurface geological formations for carbon dioxide capture and storage (CCS) offers a practical solution to address anthropogenic CO₂ emissions and mitigate global warming. Depleted oil and gas reservoirs are promising storage sites based on preliminary studies, owing to their well-understood and proven capacity to store hydrocarbons over millions of years. However, implementing CCS in these reservoirs poses challenges, concerning CO₂ injectivity and maintaining well integrity. One significant obstacle encountered during CO₂ injection in depleted gas reservoirs is the formation of CO₂ hydrates. This process involves the conversion of liquid/gas CO₂ into CO₂ hydrate inside the well tubing or nearby zones due to the cooling effect arising from the isenthalpic expansion of CO₂, known as the Joule-Thomson effect. Among the various factors influencing the risk of CO₂ hydrate formation during injection, the salt content of reservoir brine is one that substantially impacts both the thermodynamic and kinetic aspects of hydrate. Besides salt drop-out/precipitation near the wellbore due to the water-to-hydrate conversion can impede CO₂ injectivity in gas-depleted reservoirs, the salt content of brine also plays a role in water activity, leads to a reduction in CO₂ solubility and promote CO₂ hydrate formation. Despite a comprehensive understanding of this mechanism in bulk, the specific influence of salt type and concentration on CO₂ hydrate formation and dissociation in porous media, as well as their impact on permeability, remains unclear. This study aims to investigate the impact of brine containing different concentrations of NaCl and CaCl₂ on water-to-hydrate conversion, rate of CO₂ consumption, and CO₂ hydrate saturation. The results from this study provide a new perspective on assessing and predicting permeability impairment in the near wellbore region due to CO₂ hydrate formation and its implications on CO₂ injectivity. The experimental findings indicate a reduction in water-to-hydrate conversion with an increase in the salt concentration of the solution. Moreover, CaCl₂ solutions exhibit a relatively longer induction time compared to NaCl solutions. In both sets of experiments involving NaCl and CaCl₂, there is a noticeable decline in permeability when water hydrate memory is present as salinity increases. Nevertheless, the reduction in permeability is significantly less pronounced in CaCl₂ experiments compared to NaCl, attributed to the higher re-dissolution of CaCl₂ in the water produced after hydrate dissociation.

Keywords: CO₂ storage, Depleted gas reservoirs, CO₂ hydrate, Salinity, Injectivity

A novel high-pressure acoustic apparatus to investigate gas hydrate formation and distribution in porous media

Constant Agnissan¹, Livio Ruffine^{1, 3}, Marco Terzariol¹, Pascal Pelleau¹, Damien Le Vourc'h², Xavier André², Tadios Quinios¹, Antoine Jean¹, Olivia Fandino¹

¹ Ifremer, Univ Brest, CNRS, UMR Geo-Ocean, F-29280 Plouzané, France

² Ifremer, RDT, F-29280 Plouzané, France

³ IFPEN, 92852 Rueil-Malmaison Cedex, France

There is a growing interest to investigate the mechanisms and processes of hydrate accumulation and distribution in porous media. From a Earth Science point of view, natural gas hydrates encountered in marine sediments and in the Permafrost are prone to trigger landslide or slope instability¹. There are also sensitive to climate change, which may lead to their partial decomposition with potential methane transfer to the water column and the atmosphere². Therefore, it is key to investigate how the nature of the porous medium can affect their formation and distribution to better located both massive accumulations and vulnerable hydrates. Thus, extensive nature-mimicking laboratory studies, have been carried out to get insights on the influence of sedimentary matrices on hydrate formation and the resulting physico-chemical properties.

In this context, an experimental set-up with a custom-designed high pressure cell (Fig.1) was developed to study hydrate formation and distribution from a ~22 cm length sediment core. The apparatus allows simulating vertical fluid transport processes within the porous matrix, with controlled changes in the sediment compaction (vertical effective stress) as in natural environments. The cell hosting the sediment is equipped with 12 temperature sensors at different positions to map the temperature anomalies within the core during hydrate formation. Eight pairs of acoustic sensors, operating with the bender/extender elements technique³⁻⁴, are strategically positioned along the cell wall to measure the elastic wave velocity in the medium, thereby provide additional mapping of the hydrate distribution within the sediment core by detecting the transition from gas/liquid to hydrates based on abrupt changes in wave velocity. In a first part, this work presents all the details of the new experimental set-up. Here, we present a detail description of the novel experimental set-up, together with our preliminary results on the study of methane hydrate formation in silica sand.



Figure 1. 3D image of the high-pressure acoustic cell

1. Sultan, N.; Cochonat, P.; Foucher, J. P.; Mienert, J., Effect of gas hydrates melting on seafloor slope instability. *Marine Geology* **2004**, 213 (1), 379-401.
2. Ruppel, C. D.; Kessler, J. D., The interaction of climate change and methane hydrates. *Reviews of Geophysics* **2017**, 55 (1), 126-168.
3. Lee, J.-S.; Santamarina, J. C., Bender Elements: Performance and Signal Interpretation. *Journal of Geotechnical and Geoenvironmental Engineering* **2005**, 131 (9), 1063-1070.
4. Hu, G.-W.; Ye, Y.-G.; Zhang, J.; Diao, S.-B.; Liu, C.-L., Acoustic Properties of Hydrate-Bearing Unconsolidated Sediments Measured by the Bender Element Technique. *Chinese Journal of Geophysics* **2012**, 55 (6), 635-647.

Exploring the Minimum Detectable Concentration of Methane Hydrate Using Associated Alpha Particle Technique

Josip Batur^{1*}, Davorin Sudac¹, Ilker Meric², Vladivoj Valkovic¹, Zeljko Orlic¹, Karlo Nad¹,
Jasmina Obhodas¹

¹ Rudjer Boskovic Institute, Bijenicka c.54, 10000 Zagreb, Croatia

² Department of Computer Science, Electrical Engineering and Mathematical Sciences, Western
Norway University of Applied Sciences, 5020 Bergen, Norway

*jbatur@irb.hr

In relatively recent times it has come to light that methane hydrate (MH) deposits exist on a global scale, both within permafrost regions and oceans. Currently, it is understood that these solid crystalline compounds, where CH₄ molecules are incorporated into water ice lattices hold potential as an huge energy source, possibly supplementing conventional hydrocarbon reserves worldwide. For instance, methane hydrate was recently successfully used as a rocket fuel for Odysseus and is proven to be more efficient and environmentally friendlier than conventional rocket propellants. Furthermore, MH deposits may be susceptible to climate fluctuations, as evidenced by geological records indicating significant consequences for global ecosystems in the Earth's past. Therefore, further advancement in sophisticated techniques is imperative to enhance our capacity for characterizing, quantifying, and monitoring MH reserves. In the present study, the minimum detectable concentration (MDC) for methane hydrate was investigated utilizing 14 MeV neutrons in conjunction with the associated alpha particle method (AAP). The results were obtained for different quantities of methane hydrate simulant present in the target sample, along with varying measurement times. Additionally, Monte Carlo simulations of the experiment were conducted to verify the experimental findings.

Unraveling the dynamics of gas hydrate formation and methane migration in the western Black Sea: Insights from a basin-scale numerical model

Ewa Burwicz-Galerie¹, Matthias Haeckel², and Klaus Wallmann²

¹ MARUM – Center for Marine Environmental Sciences, University of Bremen, Leobener Str. 8, 28359 Bremen, Germany, eburwicz-galerie@marum.de

² GEOMAR Helmholtz Centre for Ocean Research Kiel, Wischhofstr. 1-3, 24148 Kiel, Germany

The distribution of basin-scale gas hydrates and methane migration pathways in the western Black Sea remain enigmatic, owing to the region's complex geological history. Characterizing these abundant gas hydrate systems across temporal scales poses significant challenges. In this study, we developed and applied a 3D large-scale numerical model to study the formation, development, and fate of natural gas hydrate systems in the western Black Sea sub-basin. Our model enables us to simulate the dynamic evolution of basin geometry and facies distribution over the past 98 million years.

Our findings reveal three distinct mechanisms driving gas hydrate formation within the reconstructed sub-basin: gas hydrate recycling zones, chimney-like vertical transport structures, and gas hydrate deposits associated with paleo-deep sea fans. Here, we present the modeling evidence for complex migration pathways represented by the following end-members: short-distance migration related to mass transport deposits (MTD), mid-distance migration alongside the carrier beds associated with the paleo-channels, and long-distance migration from open basin towards the coastal areas.

The first part of our study focuses on predicting the total volume of gas hydrates stored within western Black Sea sediments under the present-day conditions. Subsequently, we conduct a detailed analysis of regional gas hydrate systems, focusing on the Dniepr and Danube fan systems (S1 – S5 channels, including the major Viteaz canyon), multiple offshore locations in Turkey (i.e. offshore Istanbul, Akçakoca, and Amasra, and in the Sakarya Canyon), and the central Black Sea area.

Furthermore, we investigate various biogenic methane formation kinetics and their impact on basin-scale methane generation. Our sensitivity studies enable us to predict the optimal temperature range for microbial activity driving methanogenesis in the Black Sea sediments. Overall, our study provides a novel understanding and quantitative correlation between methane generation, migration, and storage in the form of gas hydrates on a basin-scale in the western Black Sea.

Subsurface heat, salt and other inhibitors of methane hydrate stability in the Mediterranean Basin

Angelo Camerlenghi¹, Cristina Corradin^{1,2}, Umberta Tinivella¹, Michela Giustiniani¹, Claudia Bertoni³

¹ National Institute of Oceanography and Applied Geophysics, OGS, Trieste, Italy
acamerlenghi@ogs.it

² Department of Mathematics, Informatics and Geosciences, University of Trieste, Trieste, Italy

³ Department of Earth Sciences - University of Oxford, Oxford, U.K.

Despite the expected presence of gas hydrates from modelling studies, the land-locked Mediterranean Basin displays a lack of evidence of extensive gas hydrate presence from samples and seismic data. Despite several attempts to understand the gas hydrate system, the Mediterranean lacks an assessment of its gas hydrate potential that considers measured thermohaline properties of interstitial waters. With the purpose of improve our understanding of the gas hydrate potential of the Mediterranean Basin margins, we considered the full spectrum of available physical and chemical parameters and undertook a basin-wide approach to the modelling of the Methane Hydrate Stability Zone (MHSZ).

Water column thermohaline properties are from measurements and model grids. Subsurface temperature and salinity in pore waters are from 44 Deep Sea Drilling Project (DSDP) and Ocean Drilling Program (ODP) boreholes. The stability field of methane hydrate is simulated as a function of *in situ* pressure, temperature, and salinity using the equation of state of Moridis (2014) in each of the 44 boreholes and in the water column.

The modelled intersection of the top of the MHSZ with the seafloor ranges from 1163 m to 1391 m below sea level, considerably deeper than in world continental margins. An important anomaly exists in the thickness of the MHSZ with respect to that calculated with constant pore-water salinity equal to bottom-water salinity (as much as ~ -300 m, 85%). The anomaly is produced by important positive pore-water salinity anomalies, indicating the pervasive presence of brines with concentrations of halite and gypsum as high as saturation (>300‰) found in 33 of the 44 boreholes analysed.

The pervasive presence of high-salinity pore waters, coupled with the unique warm and salty water column inhibit the formation of gas hydrates. Messinian salt giant deposits, whose distribution coincides well with that of the areal distribution of the modelled MHSZ, act as an additional important inhibitor of the formation of pervasive gas hydrates in the subsurface because of halite sealing capacity with respect to upward hydrocarbon gas migration into the MHSZ. Bypass of the Mediterranean salt seal by subsalt gas occurs only through locally focused fluid migration paths, including mud volcanoes where gas hydrates have been detected. Therefore, the Mediterranean salt giant acts as an important regional scale limiting factor to the formation of gas hydrates.

Finally, ODP Leg 160 and Leg 161 boreholes demonstrates that the pore-water chemistry expected above the Messinian evaporitic layer is unfavourable to *in situ* organic matter fermentation and methanogenesis and acts as a further limiting factor to the generation of gas hydrates in the MHSZ.

We conclude that the Mediterranean Basin, hosting the youngest salt giant on Earth, is not prone to the widespread formation and preservation of gas hydrates in the subsurface and that the gas hydrate potential of salt-bearing rifted continental margins may be considerably decreased by the presence of subsurface brines.

Direct hydrate-based CO₂ sequestration in marine environments: lessons learned from CO₂-CH₄ replacement in natural gas hydrates

Beatrice Castellani^{1,*}, Andrea Nicolini¹ and Federico Rossi¹

¹ *Department of Engineering, University of Perugia, Via G. Duranti 67, 06125 Perugia (Italy)*

The focus of this paper is on the study of clathrate hydrates for direct CO₂ sequestration in marine environments as a potential countermeasure for global warming. Unlike traditional geological sequestration methods, which involve replacing methane with CO₂ in natural gas hydrate (NGH) reservoirs, this approach involves directly forming CO₂ hydrates in the marine environment. The favorable properties of CO₂ hydrates, such as higher density than seawater, stability under moderate pressure and temperature conditions, solid storage form, cementing effect in porous sediments, and slower dissolution of CO₂ in surrounding water, make this method promising.

The paper aims to explore the feasibility of hydrate-based CO₂ storage compared to conventional geological options, starting from the lesson learned from the experimental investigations on the CO₂-CH₄ replacement process in NGH. In particular, the results of CO₂-CH₄ replacement in NGH are related to the effect of the physical and chemical nature of the sediment, the properties of water and the presence of salts. Such results are then compared to those related to pure CO₂ hydrates formation. The experimental apparatus consists of a high-pressure reactor with specific dimensions placed within a thermostatic bath filled with water and glycol, cooled by a chiller for temperature control.

The aim of this work falls within the PRIN 2022 PNRR project entitled «Reliable long-term CO₂ storage as clathrate hydrates in seawater and marine sediments (CO₂-RESTO)», funded by the European Union – Next Generation EU and led by the University of Perugia, the University of Camerino, and the OGS Institute as a research units.

Image-based pore network model to investigate hydrate pore habit effect on dynamic permeability evolution in hydrate-bearing sediments

Mingqiang Chen^{1,2,3}, Qingping Li^{1,2,3}, Weixin Pang^{1,2}, Qiang Fu^{1,2}, Huiyun Wen^{1,2}, Bo Yang^{1,2},
Chaohui Lyu⁴, Yang Ge^{1,2}, Xiaohan Zhang^{1,2,3}

¹National Key Laboratory of Offshore Natural Gas Hydrate, Beijing, 10028

²Research Center of Natural Gas Hydrate and Marine Resource Strategy, Research Institute of China National Offshore Oil Corporation, 10028, Beijing

³Huairou Laboratory, Beijing, 101400

⁴Petroleum Exploration and Production Research Institute, SINOPEC, Beijing, 100083

Abstract : As a crucial parameter that determines fluid flow in hydrate-bearing sediments, dynamic permeability is significantly affected by hydrate pore habit since it directly influences fluid flow environment in porous media. However, currently employed hydrate-bearing pore networks for studying hydrate pore habit effect on dynamic permeability evolution are usually incapable of accurately characterizing the complex cross-sections of hydrate. In this work, two novel 3D dilation algorithms for generating hydrate with complex morphology and different pore habits directly into CT images are firstly proposed based on the smallest elements of voxel units. Compared with superimposed 2D dilation algorithms, these two methods can ensure the smooth transition of hydrate in 3D space, which is closer to the actual hydrate spatial distribution characteristics. Based on the two algorithms, hydrate-bearing samples with different hydrate saturation respectively in the patterns of grain-coating and pore-filling are generated and hydrate 3D spatial distribution characteristics are analyzed. Furthermore, an improved maximum ball algorithm is applied to extract hydrate-bearing network models with different hydrate saturation in each pore habit. Afterwards, the effect of hydrate occurrence on representative pore structural and connective parameters such as the effective pore throat radius, pore throat shape factor, and coordination number is investigated in detail. Subsequently, dynamic permeability at different hydrate saturation in each hydrate pore habit is calculated in terms of extracted hydrate-bearing pore networks, revealing the influence of hydrate pore habit on dynamic permeability evolution. Finally, a novel universally representative mathematical model for dynamic permeability prediction is developed. Results indicate that hydrate directly formed in CT images exhibit complex morphology. The difference of initial pore sizes leads to variations of hydrate saturation in each layer. Different hydrate pore habits in the sediments play significantly different roles in dynamic evolution of the effective pore structures such as pore throat radius, shape factor as well as the connectivity, resulting in the decline rate of dynamic permeability in the pattern of pore filling larger than that of grain coating with the increase of hydrate saturation. The novel proposed dynamic permeability prediction model matches well with the obtained permeability in different hydrate pore habits, indicating its accuracy and universality. This work plays a significant role in accurately revealing the dynamic permeability evolution with different hydrate pore habits and predicting production capacity of hydrate-bearing sediments.

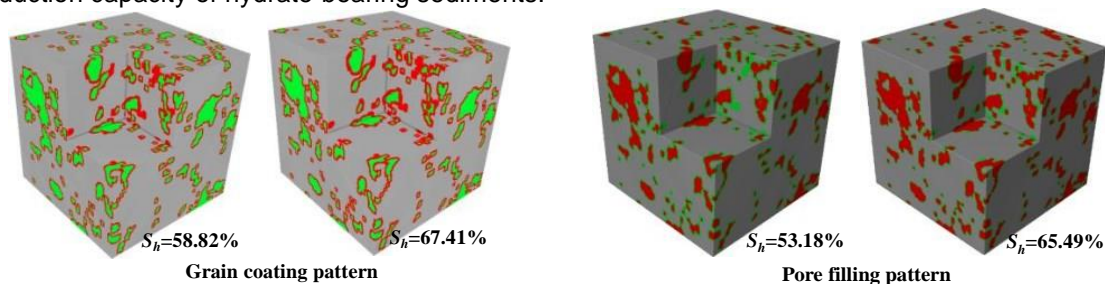


Figure 1 Hydrate-bearing digital core with different pore habits (grey-grain, light green-effective pore, red-hydrate)

Reprocessing of 2D seismic data for the search of gas hydrates in the Eastern Mediterranean region

Agnese Chies¹, Ilaria Barone¹, Umberta Tinivella², Michela Giustiniani²

¹ *Università degli Studi di Padova, dipartimento di Geoscienze, Padova (Italy),
agnese.chies@studenti.unipd.it, ilaria.barone@unipd.it*

² *National Institute of Oceanography and Applied Geophysics - OGS, Italy, utinivella@ogs.it,
mgiustiniani@ogs.it*

This work presents the reprocessing of the MS-52 2D seismic line with the purpose of detecting the possible presence of gas hydrates in the Eastern Mediterranean region, in the Nile deep-sea fan (Fig. 1). In particular, this reprocessing aims to confirm or disprove the presence of a bottom simulating reflection (BSR) in this line, already supposed in the past.

This work is based on a dataset acquired 50 years ago, when the technology of acquisition was less-advanced compared to today's equipment. Despite that, the raw data of the MS-52 line are of good quality. The reprocessing, performed with cutting-edge processing algorithms, and including shot interpolation, noise attenuation, demultiple, velocity picking, gap deconvolution and Kirchoff pre-stack time migration, notably improved the quality of the final migrated stack section, allowing a more accurate geological interpretation. The supposed BSR revealed to be a continuous lithological reflector. It cannot be defined as BSR because it is continuous, it does not mimic the sea floor, and it does not show an inverse polarity with respect to the sea floor. It is possible that gas hydrates are present in the area without showing a BSR, as recently suggested in literature. However, the presence of gas hydrates is hampered by the particular conditions of salinity, temperature and water composition in the pores. In general, the Nile deep-sea fan covers a large area, and the presence of gas hydrates is proved in a few places, but not in the region where the line MS-52 was acquired.

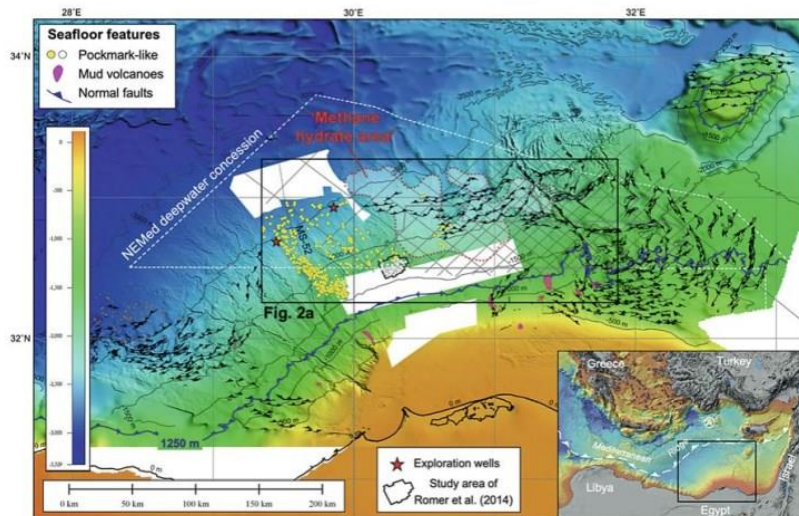


Figure 1. Bathymetric map with the location of the MS-52 line, the exploration wells Kg45-1 and Kj49-1 and 2D and 3D seismic exploration.

Exploring the efficiency of microbial anaerobic oxidation of methane as sink to hydrate-sourced methane

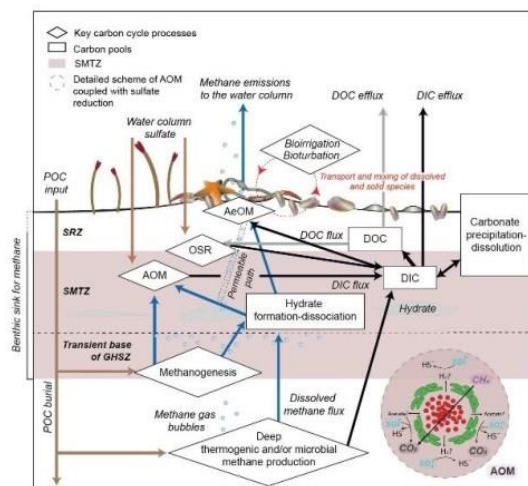
Maria De La Fuente¹, Sandra Arndt¹, Héctor Marín-Moreno², Tim A. Minshull² and Jean Vaunat³

¹ BGeoSys, Department Geoscience, Environment & Society (DGES), Université Libre de Bruxelles, 1050 Brussels, Belgium, maria.de.la.fuente.ruiz@ulb.be

² School of Ocean and Earth Science, University of Southampton, European Way, Southampton SO14 3ZH, UK

³ Department of Civil and Environmental Engineering, Universitat Politècnica de Catalunya, 08034 Barcelona, Spain

Ocean warming poses a significant threat to the stability of methane hydrates in continental margins, potentially resulting in the release of methane into marine sediments, the water column, and eventually, the atmosphere. Over timescales ranging from decades to millennia, microbially mediated anaerobic oxidation of methane (AOM) in marine sediments has been identified as a potential mechanism to mitigate methane efflux from the seafloor. However, recent studies have revealed considerable variability in the efficiency of the AOM sink. For example, in cold seep environments, AOM efficiency ranges from 80% to 20% depending on fluid flow rates, whereas in pristine seepage areas, it decreases to approximately 10%. This variability is closely linked to the balance between multiphase methane transport and the growth dynamics of microbial communities. This study utilizes a novel 1D multiphase reaction-transport model to explore the transient evolution of AOM sink efficiency and its implications for seafloor methane emissions following centennial-scale methane releases driven by climate-induced hydrate destabilization. The research investigates how gaseous methane transport, including mechanisms such as induced tensile fracturing due to pore fluid overpressure, and the dynamics of methanotrophic biomass influence the effectiveness of the AOM sink. Preliminary findings suggest that the AOM sink may have limited capacity to mitigate methane emissions in sediment-rich environments. Moreover, the slow growth rate of methane-oxidizing microorganisms could result in significant temporal windows during which methane escapes into the ocean. This integrated analysis sheds light on the intricate dynamics governing the efficiency of the benthic AOM sink in response to hydrate-derived methane. It contributes to a more thorough understanding of potential methane emissions and carbon cycling in continental margins in the context of global warming.



Geophysical evidence for gas hydrate/free gas associated with mud volcanism in the western Ross Sea (Antarctica)

Riccardo Geletti¹, Martina Busetti¹, Giuseppe Brancatelli¹, Dario Civile¹, Chiara Sauli¹, Edy Forlin¹, Vincenzo Lipari¹

¹ National Institute of Oceanography and Applied Geophysics - OGS, Trieste (Italy), rgeletti@ogs.it -

Geophysical evidence of gas hydrates associated with mud volcanism has been found in the western Ross Sea (Geletti & Busetti, 2011, 2022; Busetti et al., 2024). The location of the mud volcanoes appears to be closely related to the tectonic structures in this area (Sauli et al., 2021) and the fluid releases, with the zone where Bottom Simulating Reflectors (BSRs) are strongly pronounced in the seismic profiles. These BSRs describe the transition between gas hydrate and free gas. The presence of the reservoir appears to be associated with morpho-structural high zones that may act as traps for the gas, which is present in both the solid and gaseous phases. Mud volcanism is generally involving voluminous generation and emission of methane and carbon dioxide, which means that most mud volcanoes serve as an efficient, natural source of greenhouse gasses and consequently play an important role in global climate dynamics (Judd, 2005). The system of mud volcanoes and gas-bearing sediments in the western Ross Sea could therefore be a source of methane flux from the lithosphere to the hydrosphere and atmosphere, as recent studies along the coastal margin have also shown (Seabrook et al., 2023), and thus impact on the greenhouse effect and climate change.

We present a reprocessing of multichannel seismic profiles that provides evidence for a plumbing system feeding the mud volcanoes, with gas leaking from the seafloor in the western Ross Sea (Geletti and Busetti, 2011, 2022, Busetti et al., 2024). In pre-stack analysis, BSRs in the seismic records are characterized by several anomalies in amplitude, velocity and frequency compared to the normal adjacent seismo-stratigraphic reflectors (Geletti & Busetti, 2011, 2022): (a) the amplitude of the reflection varies with offset, with its negative value increasing with distance (or incidence angle) and absolute values comparable to those of the seafloor reflection; (b) the velocity function at the level of the BSR decreases drastically, going from about 2000 m/s to less than 1400 m/s in the underlying layer; (c) the dominant frequency of the BSR is below 25 Hz of the seismostratigraphic reflectors at the same time twt. On the stacking profiles, the BSRs appear with events of strongly negative amplitude, simulating the trend of seafloor deepening with increasing bathymetric depth, cutting the horizons in some areas regardless of stratigraphy. These BSRs are discontinuous and are interrupted near some active faults in the Lee Arch (acoustic gap), at the top of which morpho-bathymetric reliefs and depressions such as mud volcanoes and pockmarks can be recognized.

- Busetti, M., Geletti, R., Civile, D., Sauli C., Brancatelli G., Forlin E., et al. (2024). Geophysical evidence of a large occurrence of mud volcanoes associated with gas plumbing system in the Ross Sea (Antarctica). *Geos. Frontiers*, 2024, 15(1), 101727. <https://doi.org/10.1016/j.gsf.2023.101727>
- Geletti, R., & Busetti, M., (2022). *Bottom Simulating Reflector in the western Ross Sea, Antarctica*. In: Mienert, J., et al., (Eds), *World Atlas of Submarine Gas Hydrate in Continental Margins*, 475-482. https://doi.org/10.1007/978-3-030-81186-0_40
- Geletti, R., & Busetti, M. (2011). A double bottom simulating reflector in the western Ross Sea, Antarctica. *J. of Geophysical Research*, 116, B04101, <https://doi.org/10.1029/2010JB007864>
- Judd, A. (2005). *Gas emissions from mud volcanoes. Significance to Global Climate Change*. In Martinelli G., Panahi B., (ed.) *Mud Volcanoes, Geodynamics and Seismicity*, 51(4), 147-157.
- Sauli, C., Sorlien, C., Busetti, M., De Santis, L., Geletti, R., Wardell, N., Luyendyk, B.P., (2021). Neogene development of the Terror Rift, western Ross Sea, Antarctica. *3G*, 22/3, 1-20. <https://doi.org/10.1029/2020GC009076>
- Seabrook, S., Law, C., Thurber, A., Ladroit, Y., Cummings, V., Tait, L., et al. (2023). Emergent Antarctic seafloor seeps: A tipping point reached? *Nature portfolio*. <https://doi.org/10.21203/rs.3.rs-3657723/v1>

Kinetic Study of Binary Gas Mixtures for Understanding Mechanism of Hydrate Formation in the Sea of Marmara: Experimental and Molecular Dynamics Simulation Approaches

A. Heidari¹, Á. M. Fernández-Fernández², O. Fandino¹, M. Pérez-Rodríguez², M. M. Piñeiro², M. Tariq³, L. Ruffine^{1,4*}

¹ Geo-Ocean, Univ Brest, CNRS, Ifremer, UMR6538, F-29280 Plouzane, France

² Dpto. de Física Aplicada, Univ. de Vigo, 36310, Spain

³ LAQV, REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

⁴ IFPEN, 1-4 Av. du Bois Préau, 92852 Rueil-Malmaison, France

*Corresponding author e-mail: livio.ruffine@ifpen.fr, atousa.heidari@ifremer.fr

This study aims to advance our understanding of the mechanisms of complex-hydrate formation within the hydrate deposits of the Sea of Marmara (SoM). The SoM, situated at the western end of the northern branch of the North Anatolian Fault (NAF), is an inland sea with significant geological importance due to the NAF's seismic activity. Cold seeps, where gas venting is common, are frequently observed along this major fault network [1]. The analysis of gas bubbles and thermogenic hydrate samples collected on the Western High [2, 3] reveals the presence of complex (multicomponent) gas mixtures, containing mainly methane (66-88%). Notably, it shows the highest concentrations of propane (18.8%) and isobutene (9.5%) in hydrate samples ever recorded to date, in contrast to their lower concentrations in gas bubbles (2.85% propane and 0.88% isobutene) [2].

Here, we focus on the influence of non-methane hydrocarbons as well as various compositions of hydrocarbon components on the kinetics of complex hydrate formation. To address this issue, we applied a methodology that combines high-pressure kinetic experiments with theoretical approaches (modeling and Molecular Dynamic (MD) simulation). Hence, the first part of this study details the kinetic experiments conducted on binary gas mixtures including the calculation of key kinetic parameters such as the induction time, kinetic constant, amount of gas consumed, and the conversion of water to hydrate.

The second part involves the MD simulations to understand the effect of gas composition and driving force on the kinetic behavior of the complex hydrate at molecular levels. Therefore, the GROMACS (version 2020.1) has been used in the isothermal-isobaric (NPT) ensemble, under conditions that closely replicate those applied in the experiments. In this simulation, water and gas components have been described using the TIP4P/Ice model and united atoms force fields, respectively. The simulation results for type sII hydrates are then compared with experimental data, forming a comprehensive analysis that bridges theoretical predictions with experimental observations.

Keywords: Sea of Marmara, Gas mixture kinetics, complex hydrate formation, and MD simulation.

1. Bourry, C., et al., *Free gas and gas hydrates from the Sea of Marmara, Turkey: Chemical and structural characterization*. Chemical Geology, 2009. 264(1-4): p. 197-206.
2. Ruffine, L., et al., *Multiple gas reservoirs are responsible for the gas emissions along the Marmara fault network*. Deep Sea Research Part II: Topical Studies in Oceanography, 2018. 153: p. 48-60.
3. Ruffine, L., et al., *Multidisciplinary investigation on cold seeps with vigorous gas emissions in the Sea of Marmara (MarsiteCruise): Strategy for site detection and sampling and first scientific outcome*. Deep Sea Research Part II: Topical Studies in Oceanography, 2018. 153: p. 36-47.

Fabrication of silica gel-clathrate hydrate composite for improved CO₂ storage efficiency

Siyoon /Jeong¹, Jeong-Hoon /Sa²

¹ *Department of Chemical Engineering, Dong-A University, Busan, South Korea, 2471092@donga.ac.kr*

² *Department of Chemical Engineering, Dong-A University, Busan, South Korea, jhsa@dau.ac.kr*

The accelerating pace of global warming is causing rapid climate change crisis in recent times, and thus carbon capture, utilization, and storage (CCUS) technology are gaining prominence as key solutions. As the CCU technology would take considerable time to be actually used in our daily lives, there is a growing interest in CO₂ storage technology. In this work, we studied on a sustainable solution for CO₂ storage in the form of solid clathrate hydrate in deep-sea environments. In addition, we aimed to enhance the stability of CO₂ ocean storage by fabricating clathrate hydrate-silica composites instead of directly injecting captured CO₂ into the deep sea environment through pipelines. To fabricate clathrate hydrate-silica composites, we utilized nano porous silica gel as the porous material. While the use of nano-sized pores of silica gel would slightly shift the phase equilibrium conditions of hydrates to higher pressures regions, their use also has the advantages of significantly increasing the interfacial contact area between gas and liquid, allowing for faster and more efficient formation of clathrate hydrates. Our research involved varying parameters such as silica gel particle size, pore diameter, water saturation, surface properties, and the concentration of the L-tryptophan (L-trp), which is a promoter that can enhance CO₂ hydrate formation kinetics. The experimental results showed that smaller particle size and larger pore diameter led to higher values in CO₂ uptake upon hydrate formation and water to hydrate conversion. Additionally, we compared CO₂ uptake and conversion with different water saturation levels of 60%, 80%, 100%, and 210% to find out its effect on hydrate formation kinetics. According to the results, a sharp decrease in hydrate formation kinetics with water saturation of 210%, where the space between silica gel particles outside the pores were filled with water, limiting mass transfer during hydrate formation. We also used the environment friendly L-trp as a promoter for CO₂ hydrate formation to minimize potential environmental pollution in deep sea area. The effect of the L-trp concentration (100 ppm, 300 ppm, 1000 ppm) on CO₂ hydrate formation in the silica gel was investigated. It was found that while there was no significant promotion effect at 100 ppm, CO₂ uptake and water to hydrate conversion increased with L-trp concentrations. Based on our results, an efficient strategy for utilizing clathrate hydrates formed with silica gel for ocean storage of CO₂ was proposed. Our findings are expected to contribute not only to the design of an efficient process for manufacturing clathrate hydrate-silica gel composites but also to serve as the foundation of CO₂ ocean storage technology.

Effects of Methane Hydrate Phase Transition on Deformable Sediment Structure Evolution under Cold Seep System

Xuan Kou¹, Yi Wang¹, Yu Zhang¹, Gang Li¹, Zhao-Yang Chen¹, Xiao-Sen Li¹
¹ Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou, China,
 lixs@ms.giec.ac.cn

As an important way of methane cycling on the Earth, the cold seeps are often accompanied by the occurrence of methane hydrates. Cold seeps under seafloor manifests the migration of methane-rich fluid from the sedimentary subsurface to the seabed and into the water column, and even reach the atmosphere. However, the interaction influencing mechanism between methane hydrate phase transition and methane-rich fluid seepage in deformable subsurface marine sediments are still lacking knowledge.

In this work, we firstly realized the microscale controllable process of methane hydrate phase transition in fine grained clayey sediments collected from the active cold seep area in South China Sea. By advanced X-ray Computed Tomography technology, we successfully acquired the dynamic hydrate phase transition behaviors and its effects on sediment structure evolution and solid migration. The new phenomena of pore generation during hydrate formation and pore enlargement during hydrate dissociation have been observed, resulting in unpredictable damage to the sediment structure. We further investigated the controlling mechanism of solid migration, which is the critical factor in determining sand production of hydrate exploitation or potential geohazards. In-depth discussions suggest that the structure change and solid migration might enhance hydrocarbon fluid flow to the shallow seafloor, affecting local ecosystems of the cold seep areas and global environment. **These findings could provide valuable information for hydrate-related greenhouse gas emission evaluation in cold seep areas.**

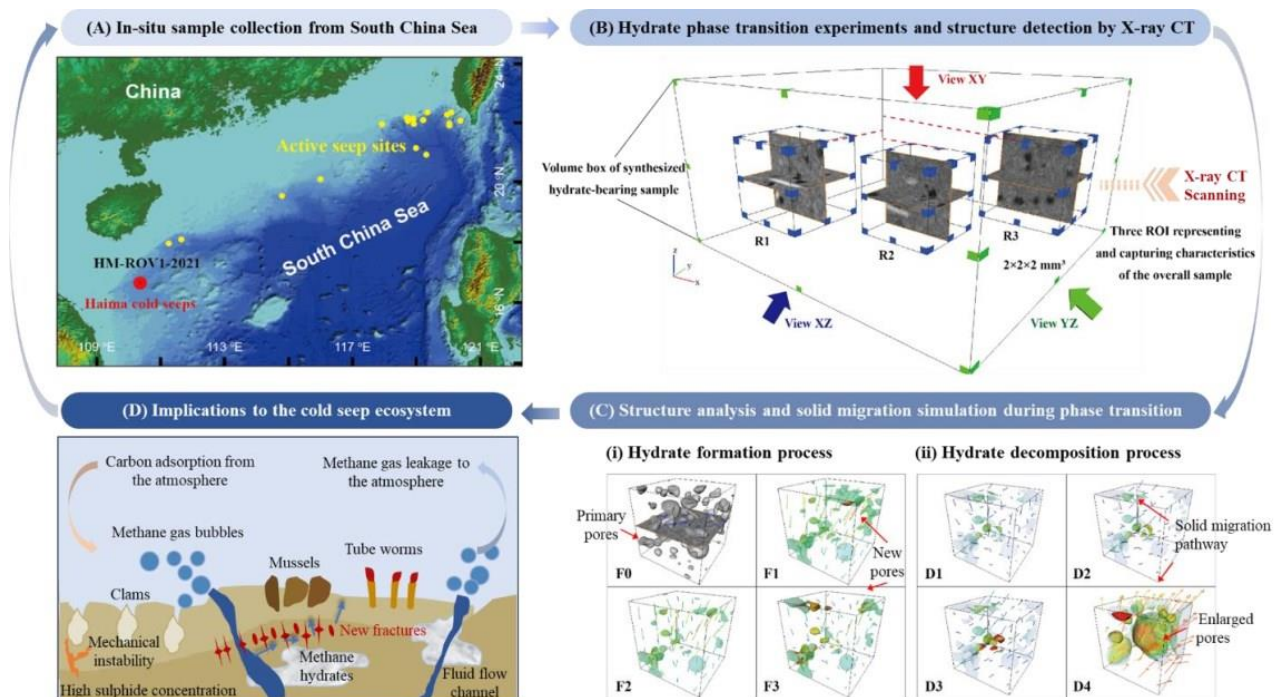


Figure 1. Schematic of experimental process and implications of results to the cold seep ecosystem

Seafloor Pockmarks on the Chatham Rise, New Zealand – Could CO₂ Hydrate be Involved in Their Formation?

Pecher, Ingo^{1,2}, Stott, Lowell³, Coffin, Richard¹, Macnaughtan, Michael², Warnke, Fynn², Strachan, Lorna², Hillman, Jess⁴, Davy, Bryan⁴, Bialas, Joerg⁵

¹Texas A&M University-Corpus Christi, Corpus Christi, TX 78412, USA, ingo.pecher@tamucc.edu

²The University of Auckland, Auckland, New Zealand

³University of Southern California, Los Angeles, CA 90089, USA

⁴GNS Science, Lower Hutt, Wellington, New Zealand

⁵GEOMAR Forschungszentrum, Kiel, Germany

An area of >50,000 km² on the Chatham Rise east of New Zealand is covered by seafloor and buried pockmarks. These pockmarks appear bathymetrically constrained. Buried pockmarks seem to have formed around glacial-stage maxima. This observation led to the hypothesis that pockmark formation is linked to sea-level low-stands, potentially involving pressure-related hydrate dissociation. An involvement of methane hydrate, however, is unlikely based on extremely low methane flux rates inferred from pore water profiles¹. Intriguingly, $\Delta^{14}\text{C}$ excursions suggest a release of geologic carbon around the last glacial termination. This carbon is hypothesized to have been released in the form of CO₂ originating at limestone sequences on top of the Hikurangi Plateau, a large igneous province that was partially subducted beneath the Chatham Rise during the Late Cretaceous². It is unclear, however, what mechanism could modulate such a release of CO₂.

Recent analyses of pseudo-three dimensional TOPAS sub-bottom profiler data³ generally confirm the link between pockmark formation and glacial-stage maxima. Phase boundary considerations would make repeated formation and dissociation of CO₂ hydrate a candidate for episodically sequestering and releasing CO₂ or for CO₂ hydrate to form an ephemeral seal for fluid release. However, to date we do not have any more direct evidence for an involvement of CO₂ hydrate in pockmark formation.

We present results from thermal analyses of bottom simulating reflections (BSRs) observed on the flanks of the Chatham Rise. On its northern flank, thermal gradients assuming methane hydrate BSRs reach 0.05-0.06 K/m, higher than previously predicted. An assumption of pure CO₂ hydrate would result in thermal gradients of 0.03-0.04 K/m, in line with more commonly used values for the study area. We also investigate the stability of mixed methane-CO₂ gases. South of the Chatham Rise in the Bounty Trough, a BSR has been detected which, if assuming methane hydrate, leads to a predicted thermal gradient of 0.06 K/m. Our results emphasize the need for additional geothermal data on the Chatham Rise to further investigate the potential involvement of CO₂ hydrate in pockmark formation.

- (1) Bialas, J.; Klaucke, I.; Mögeltönder, J. *FS Sonne Fahrtbericht / Cruise Report SO 226 CHRIMP*; GEOMAR: Kiel, 2013; Vol. 7.
- (2) Stott, L.; Davy, B.; Shao, J.; Coffin, R.; Pecher, I.; Neil, H. L. R.; Blanke, S. CO₂ Release from Pockmarks on the Chatham Rise-Bounty Trough at the Glacial Termination. *Paleoclimatol. Paleoclim* **2019**, *34* (11), 1726–1743. <https://doi.org/10.1029/2019PA003674>.
- (3) Warnke, F.; Pecher, I. A.; Hillman, J. I.; Davy, B.; Woelz, S.; Gorman, A. R.; Strachan, L. J. Pseudo-3D Cubes from Densely Spaced Subbottom Profiles via Projection Onto Convex Sets Interpolation: An Open-Source Workflow Applied to a Pockmark Field. *Geophysics* **2023**, *88* (6), 1–90.

Temporal variability of the stability field of methane hydrates in the oceans

Leonardo Riccucci¹, Angelo Camerlenghi¹, Stefano Salon¹, Umberta Tinivella¹

¹*Istituto Nazionale di Oceanografia e di Geofisica Sperimentale, Sgonico (TS) – Italia, lriccucci@ogs.it, acamerlenghi@ogs.it, ssalon@ogs.it, utinivella@ogs.it*

Climate change is mainly monitored at the Earth's surface. However, it is well known that as part of ongoing climate change, ocean circulation is also changing, and therefore the ocean floor is also subject to temperature changes. In this study, the depth of the global methane hydrate stability zone was assessed by analyzing its changes over the period from 1993 to 2018 to investigate the effect of climate change on the stability of methane hydrates. Indeed, seafloor sediments are often permeated by a methane hydrate phase, the stability of which depends on the pressure and temperature field, among other parameters, and any changes in temperature conditions near the seafloor can bring the methane hydrate into unstable conditions. The data needed for the assessment of methane hydrate stability were obtained from The Global Ocean Physics Reanalysis data set (GLORYS12V1), produced under the European Copernicus Marine Environment Monitoring Service (CMEMS), and GEBCO- The General Bathymetric Chart of the Oceans. The data were then processed with original data processing software developed in Fortran and Python languages. A quantitative estimate of the amount of methane released into ocean masses by the dissociation of methane hydrate in shallow sediments over the period under consideration was also obtained. The release of large amounts of methane could have an impact on submarine geological hazards, such as submarine landslides, and the eventual reaching of the atmosphere by methane would reinforce ongoing climate change.

Storage of methane and carbon dioxide in sediments

Daria Sergeeva¹, Murtazali Yarakhmedov^{1,2}, Anton Semenov², Vladimir Istomin¹
Andrey Stoporev²

¹ Skolkovo Institute of Science and Technology (Skoltech), Moscow, Russia, darina2010@mail.ru ²
Gubkin University, Moscow, Russia, stopor89@bk.ru

Natural gas hydrates are a widely available and high-density energy source. Studies indicate that sediments containing hydrates are typically made up of clay minerals, sand, organic material, and saltwater. This composition can be utilized to create temporary gas storage facilities in hydrate form, which can reduce the costs of disposal and logistics for exhausted and new productive horizons. To improve the efficiency of CO₂ utilization, it is important to conduct experimental modeling of hydrate formation and decomposition in various clay deposits. This will help to analyze the risks and avoid technological complications when injecting CO₂ into low-temperature formations. Indeed, when fluids are pumped into low-temperature formations, it becomes more challenging to prepare and transport the gases due to the risks of precipitation of aqueous phases (liquid water, ice, and gas hydrates) from the vapor phase during their transportation and subsequent injection. The precipitation of water or hydrates from the vapor phase can activate corrosion processes in pipelines and decrease the intake capacity of injection wells. Therefore, the proposed research aims to address these challenges and ensure that the transportation and injection of gases are carried out safely and efficiently.

This research gathered data on the formation of methane and carbon dioxide hydrates from water-saturated clay deposits with varying compositions and pressure. The study shows that hydrate formation occurred mainly from the least firmly bound water for kaolinite and bentonite samples. The low degree of conversion of water into hydrate for bentonite samples was due to the blocking of the free water-gas contact surface by the growing hydrate. However, for kaolinite, the conversion of water to hydrate was high, indicating good availability of adsorbed water for hydrate formation. Montmorillonite samples showed that methane hydrate formed decomposed over the entire temperature range due to the formation of a significant part of the hydrate from interlayer water. The X-ray powder diffraction patterns showed the presence of significant amounts of ice in all samples. The findings revealed that a developed water-gas surface enables high-speed and reproducible parameters of the hydrate formation process. This is crucial for increasing the efficiency of hydrate technologies. The results also provide insight into the behavior of gas hydrates in porous media and may help assess the stability of gas hydrates in clayey sediments.

This work was supported by the Russian Science Foundation (grant 23-79-01312)

[1] Wu, Z., Liu, W., Zheng, J., and Li, Y., 2020. Effect of methane hydrate dissociation and reformation on the permeability of clayey sediments. *Applied Energy*, 261, p.114479.

Dynamic of the gas hydrate/free gas system based on geophysical analysis and paleo-BSR modeling

Ivan Vargas-Cordero¹, Umberta Tinivella², Michela Giustiniani², Lucia Villar-Munoz³, Nathan Bangs⁴,
Joaquim P. Bento⁵, Eduardo Contreras-Reyes³

¹ Valparaiso, Chile, lacruzvargas@gmail.com

² National Institute of Oceanography and Applied Geophysics – OGS, Italy, utinivella@ogs.it,
mgiustiniani@ogs.it

³ Departamento de Geofísica, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile,
Santiago, Chile, lucia.villar@gmail.com, edcontrr@gmail.com

⁴ Institute for Geophysics, University of Texas at Austin, Austin, TX, USA, nathan@ig.utexas.edu

⁵ The Metals Company, 10th Floor, 595 Howe Street, Vancouver, British Columbia, V6C 2T5, Canada.
joaquim.bento@metals.co

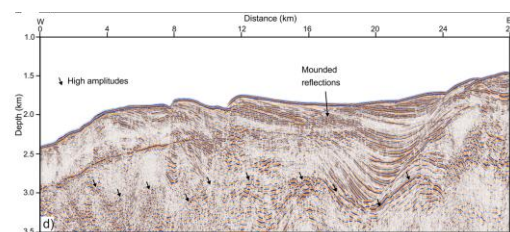
The Central-South Chile margin is an excellent site to address the changes in the gas hydrate (GH) system since the last deglaciation associated with tectonic uplift and great earthquakes. However, the dynamic of the gas hydrate/free gas (FG) system along south-central Chile is currently not well understood. From geophysical data and modeling analyses, we evaluate GH/FG gas concentrations along a seismic line, derive geothermal gradients, and model past positions of the BSR (until 13,000 years BP). The results reveal high hydrate/free gas concentrations and local geothermal gradient anomalies related to fluid migration through faults linked to seafloor mud volcanoes.

The analyzed seismic line shows large lateral variations in GH and FG. In fact, we can divide the seismic line into two distinctively different parts based on the BSR and BGR characteristics in the seismic profile. In the western part, the BSR and BGR are very clear, strong and continuous. The estimated geothermal gradient is relatively low. A structure, interpreted as a mud volcano and delimited by two faults, is associated with anomalously low hydrate concentration and relatively high geothermal gradient. In the eastern part, concentrations of GH and FG are small relative to the seaward portions of the profile, while the geothermal gradient is higher. Many faults are evident above the GH layer.

The paleo-BSR shows different behavior along the line. In the western part, it is quite coincident with the BGR, while, in contrast, it becomes shallower reaching the present BSR depth to the east. In contrast to the western part, the paleo-BSR is shallower with respect to the BGR along the eastern part, indicating an anomalously thick FG zone for an active margin.

Based on our study, we hypothesize two different dynamics in the gas hydrate/free gas system. Where the paleo-BSR coincides with the BGR, the high FG concentration in a thin layer is related to GH recycling due to climate change and geological evolution after the last glacial maximum. On the other hand, in the areas where the BGR is deeper than the paleo-BSR, supply of gas from a deep source is required to justify the thickness of FG. In presence of faults, the negligible thickness of FG is not resolved by seismic data, even if the FG is present due to the BSR detection.

In this figure, we report the pre-stack depth migrated section of the analysed seismic line. After Vargas-Cordero et al. (2021), Gas origin linked to paleo BSR, Scientific Reports 11:23960
<https://doi.org/10.1038/s41598-021-03371-z>.



Water content measurements for pure CO₂ and a CO₂-rich mixture in equilibrium with hydrates at 253 to 283 K and 3000 to 6000 psia using the DSH analytical technique.

Larissa F. Torres¹, Antonin Chapoy², Rod Burgass², Pezhman Ahmadi², Cláudio Dariva³, Frederico W. Tavares¹, Papa M. Ndiaye¹.

¹ *Programa de Engenharia Química, COPPE, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil.*

² *Centre for Gas Hydrate Research, Institute of GeoEnergy Engineering, Heriot-Watt University, Edinburgh, Scotland, UK*

³ *Núcleo de Estudo em Sistemas Coloidais (NUESC) / Instituto de Tecnologia e Pesquisa (ITP), Aracaju, Sergipe, Brazil.*

The literature presents a notable scarcity of information regarding water content measurements for systems in equilibrium with hydrates. These measurements are crucial for determining the hydrate stability zone and, therefore, essential to assess and plan potential flow assurance issues associated with water condensing from the produced stream in the pipelines. Addressing this literature gap for CO₂-rich mixtures is essential to effectively managing hydrate-related challenges in the oil and gas industry and the Carbon Capture, Utilization and Storage (CCUS) process. Despite being carried out for a long period, these measurements continue to be seen as particularly challenging due to water's high polarity. As a result, surfaces presumed to be dry often bear a thin moisture layer, complicating the quantification process. The water content can be very low at lower temperatures, making it even more difficult to accurately measure trace amounts. The calibration-free fluid-independent Differential Scanning Hydrometer (DSH) technique mirrors the Chilled Mirror method. It relies on determining dew/frost points, which are then translated into water content levels. The process involves gas transitioning from a high-pressure cell through a heated line and valve, leading to a temperature-regulated tube with electropolished interiors to avert moisture adherence and, ultimately to a moisture analyzer. The presence of water/ice is detected by frequency changes in the moisture analyzer signal. Initially, the tube's temperature is maintained sufficiently high to ensure no moisture depletion from the flow, followed by a temperature reduction beyond the frost/dew point. A decline in the analyzer signal denotes ice/dew formation within the tubes. Subsequently, the temperature is gradually elevated at a predetermined rate, with the rising analyzer signal indicating ice/water removal from the tube, signifying the instability of the solid phase. The dew/frost point temperature is identified at the temperature where the solid phase fully dissociates, and is determined by plotting the analyzer signal against the tube's internal temperature. This temperature is a point of thermodynamic equilibrium and can be converted into water content. Measurements were conducted for pure CO₂ and a CO₂ (75%) / CH₄ (25%) mixture in equilibrium with hydrates at 253, 273, 277, and 283 K. For each temperature, the measurements were made at 3000, 4000, 5000, and 6000 psia. The results were compared to literature data for validation purposes and to predictions obtained from the Cubic Plus Association (CPA) Equation of State (EoS). Experimental uncertainties were up to 5%, and the Average Deviation (ARD) from the experimental data and the CPA predictions were up to 8%.

Keywords: Gas Hydrates; Water content; Carbon Dioxide; Experimental Measurements; CPA.

Session 4: Hydrate based and energy efficient technologies

Chair: Beatrice Castellani, Nick O'Neill, Zhenyuan Yin

Sustainable CO₂ Capture in Seawater: Exploring L-Tryptophan Kinetic Promotion in Fresh and Saline Environments

Abdelhafid AIT BLAL, Ahmed OMRAN*, Valentin VALTCHEV*
Normandie Université, ENSICAEN, UNICAEN, Laboratoire Catalyse et Spectrochimie (LCS), 14050, Caen, France

Hydrate-based CO₂ sequestration (HBCS) emerges as a promising, sustainable method for long-term carbon dioxide sequestration.¹ However, the sluggish formation kinetics of CO₂ hydrates in saline systems pose a significant challenge, necessitating the exploration of strategies for process enhancement. To address this challenge, our comprehensive experimental study focuses on using an environmentally friendly amino acid as a kinetic promoter. The L-Tryptophan (L-Trp) in concentrations ranging from 0 to 2560 ppm is employed for CO₂ hydrate formation at 3.0 MPa and 275.15 K in deionized water, brine systems, and seawater. The experiments were conducted in a horizontal reactor configuration, providing enhanced surface contact between gas and liquid.

Furthermore, the *in situ* Raman spectroscopy monitoring was used to analyze molecular-level interactions and dynamics during the hydrate formation process (see Figure 1. b). The results indicate that the addition of 300, 700, 1700, and 2500 ppm L-Trp in deionized water significantly enhances CO₂ uptake by 3.4, 3.28, 3.52, and 3.28-fold, respectively, compared to the system without L-Trp.² Our induction time (IT) and t_{90} (Figure 1a) are significantly shorter than the blank and those reported by K. Jeenuang et al.² Besides a shorter IT, we observed the same uptake in a considerably shorter time period ($t_{90} = 46$ compared to 78 min). The brine system (2500 ppm of L-Trp), containing 0.5, 1, and 3 wt% of NaCl show 2.92, 2.86, and 2.32-fold higher CO₂ uptake 2.92, 2.86, and 2.32-fold with respect to the previous study.² These findings suggest potential advancements for optimizing scalable hydrate-based CO₂ sequestration technology. More details about the Raman spectroscopy investigation will be presented orally.

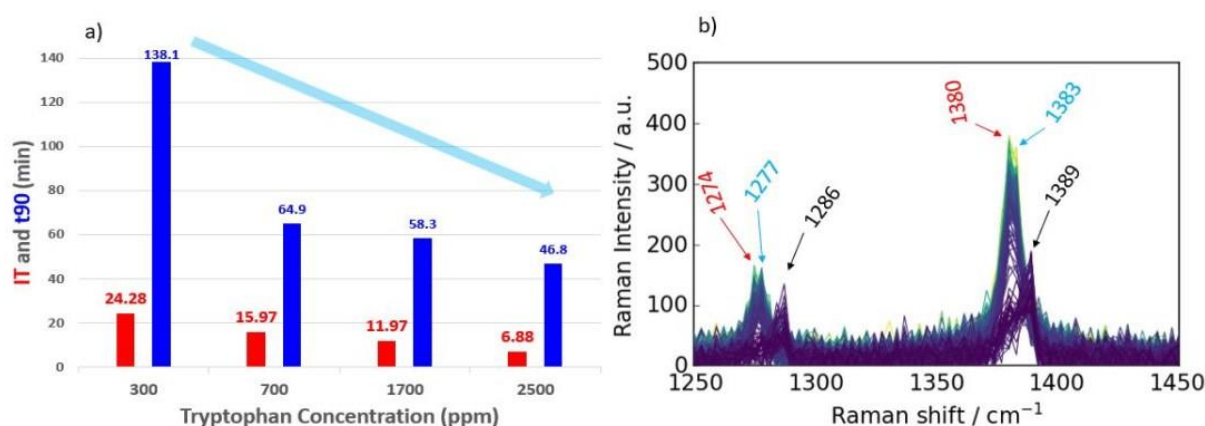


Figure 1. a) Effect of L-Trp Concentration on IT and t_{90} of CO₂ Hydrate Formation, b) Raman spectra of CO₂ hydrate formation.

1 X. Liu, Y. Li, G.-J. Chen, D.-Y. Chen, B. Sun and Z. Yin, Coupling Amino Acid with THF for the Synergistic Promotion of CO₂ Hydrate Micro Kinetics: Implication for Hydrate-Based CO₂ Sequestration, *ACS Sustainable Chem. Eng.*, 2023, **11**, 6057–6069.

2 K. Jeenuang, P. Pornaroontham, M. Fahed Qureshi, P. Linga and P. Rangsunvigit, Micro kinetic analysis of the CO₂ hydrate formation and dissociation with L-tryptophan in brine via high pressure *in situ* Raman spectroscopy for CO₂ sequestration, *Chemical Engineering Journal*, 2024, **479**, 147691.

Phase equilibrium of CO₂ and Xe hydrate crystals in presence of food products

Houaria BOUMAIZA^{1,2}, Fatou-Toutie NDOYE¹, Pascal CLAIN^{2,1}, Anthony DELAHAYE^{1,2}
¹ Université Paris-Saclay, INRAE, FRISE, Antony, 92761, France, houaria.boumaiza@inrae.fr
Léonard de Vinci Pôle Universitaire, Research Center, Paris la Défense, 92916, France

In the field of food preservation, freezing is common, but ice crystal formation and growth have some drawbacks such as losses of texture, sensory qualities and nutritional value.

Gas hydrate formation, by the specific combination of gases and water under controlled pressure and temperature conditions, have been proven to be an effective technology for addressing the preservation challenges of fresh fruits and vegetables, while maintaining their sensory characteristics. However, the mechanisms related to the formation of hydrates in fresh food products remain to be investigated and their efficacy has yet to be demonstrated in the case of frozen food products.

The purpose of this study was to investigate the potentiality of xenon and CO₂ gases to form hydrates in a food-like solution (concentrated sugar solution) and in a real porous food matrix (apple). The conditions for the formation and dissociation of CO₂ and Xe hydrates are well known in bulk phase. However, in the presence of liquid foods or a porous food matrix, data are much rarer. The use of Differential Thermal Analysis (DTA) will be used to study the mechanisms at play. The calorimetric principle of DTA, based on the temperature difference between the sample under investigation and a stable control sample, allows the determination of the latent heat of phase change and the evaluation of the hydrate fraction formed. The results have indicated that Xe hydrate formation occurs at pressures and temperatures lower than those reported in the literature, with a pressure of 0.5 MPa and a temperature of 0 °C. These results underline the significant potential of pre-freezing food products with hydrates to reduce the amount of water available for freezing and emphasise the effectiveness of this innovative approach to enhance the quality of frozen products .

Evaluation of 1,1-Difluoroethane as hydrate former for hydrate based produced water desalination

Ponnivalavan Babu and Nagu Daraboina*

*Russell School of Chemical Engineering, The University of Tulsa, Tulsa, Oklahoma 74104, USA,
e-mail : nagu-daraboina@utulsa.edu*

Acute shortage of drinking water has become one of the biggest problems facing many countries in the World. Safe and drinkable water is a necessity for survival. Hence, water resource management is needed of the hour. Desalination is the process of removal of salts and minerals from saline water or brine. Produced water (PW) is an alternative source of saline water or brine. The total volume of PW generated throughout the World is up to 39.5 million m³ per day. In United States alone, nearly 21.2 billion barrels (9.2 million m³/day) of produced water were generated during 2012. The properties of PW vary considerably depending on the type of hydrocarbon produced, geological location and formation from which it comes. The total dissolved solids of PW can be up to 300,000 mg/L. PW can be re-used after treatment for irrigation, livestock watering, aquifer storage, and municipal and industrial uses. Hydrate based desalination is a potential technology for produced water treatment. There is an ongoing effort to identify a suitable hydrate former that can operate at milder conditions and enhance the kinetics of hydrate formation.

In this study, the effect of salts present in produced water on the thermodynamics phase equilibrium of 1,1-Difluoroethane hydrate is evaluated. Different salts such as sodium chloride, sodium sulfate, magnesium chloride, and calcium chloride at various concentrations were used. We also present the process flowsheet of the hydrate based desalination process and detailed energy analysis of the process for produced water treatment.

Potential Kinetic Promoters for CO₂/CH₄ Separation: IR vs *in-situ* Raman determinations

Nadia Barbacane¹, Michele Ciulla¹, Serena Pilato¹, Rafal Damian Wolicki¹, Claire Pirim², Pietro Di Profio^{1,*}, Bertrand Chazallon^{2,*}

¹ Department of Pharmacy, University "G. d'Annunzio" of Chieti-Pescara, via dei Vestini 31, 66010 Chieti, Italy.

² Univ. Lille, CNRS, UMR 8523 – PhLAM-Physique des Lasers Atomes et Molécules, CERLA – Centre d'Études et de Recherche Lasers et Applications, F-59000 Lille, France

*Corresponding authors: B. Chazallon (bertrand.chazallon@univ-lille.fr), P. Di Profio (pietro.diprofio@unich.it)

Biogas, a renewable fuel derived from anaerobic digestion of organic waste, presents a significant potential to decreasing the dependence on fossil fuels. Unlike its non-renewable counterparts, biogas is continuously regenerated and offers a path towards a more sustainable energy production. However, prior to domestic and industrial utilization, biogas requires purification to isolate methane, the primary energy carrier, from carbon dioxide (CO₂) and trace components. Conventional CO₂ separation techniques often rely on high-pressure operations, hazardous chemicals, or energy-intensive processes [1]. Clathrate hydrates offer a safer and potentially more eco-friendly alternative. These water-based crystalline structures can trap methane molecules under slightly different conditions compared to CO₂. Interestingly, while hydrates can be a nuisance in oil and gas pipelines, their formation conditions (temperature and pressure) are relatively mild, making them a safer and easier process for biogas upgrading. Recent research suggests that using clathrate hydrates to upgrade biogas mixtures is a promising alternative to traditional methods [2]. This approach could be more economical and sustainable, avoiding the use of hazardous chemicals and making biogas a truly green energy source.

Based on a previous paper [3], several promoters are tested depending on their separation factor and occupancy. Promoters used are anionic and zwitterionic surfactants which are demonstrated to affect the hydrate-forming ability of water. Sodium lignin derivatives are also tested.

Separation experiments are conducted in the same conditions reported in the work of Di Profio et al., at a starting pressure of 2.5 MPa and 274 K, under pressure-dropping conditions. In that case, a self-assembled IR detector was used to determine the gas mixture composition before and after hydrate formation and dissociation. In the present work, Raman spectroscopy is performed to characterize the formed structures in terms of selectivity for biogas separation and hydrate occupancy under *in-situ* conditions. Raman quantification factors are used to obtain the relative amount of CH₄ and CO₂ in the hydrates, while a calibration protocol is applied to derive the relative amount of these molecules in the gas phase before and after the formation of the hydrates.

The spectroscopic results relative to the gas composition before and after hydrate formation are discussed and compared with the IR data of reference work. They show the impact of the promoters on the separation ability of clathrate hydrates, which results to be inversely proportional to the amount of gas mixture enclathrated.

Bibliography

[1] J. Das, H. Ravishankar, P.N.L. Lens. Journal of Environmental Management, 2022, 304, 114198.

[2] Q.Le, C.T. Rodriguez, L.N. Legoix, C. Pirim, B.Chazallon. Applied Energy, 2020, 280, 115843.

[3] P. Di Profio, V. Canale, N. D'Alessandro, R. Germani, A. Di Crescenzo, A. Fontana. ACS Sustainable Chem. Eng. 2017, 5, 2, 1990–1997.

Understanding the influence of TRP on the kinetics of CO₂ hydrates growth using molecular dynamics simulation

Xinrui /Cai¹, Matteo/Savalaglio², Alberto/Striolo³

¹ University College London, London, zcecxca@ucl.ac.uk

² University College London, London, m.salvalaglio@ucl.ac.uk

³ University of Oklahoma, Norman, astriolo@ou.edu

CO₂ hydrates offer opportunities in Carbon Capture, Utilisation and Storage (CCUS) due to their stability at mild operating conditions and relatively high gas storage. This work focuses on the possibility of using CO₂ hydrates to achieve affordable and environmentally friendly carbon capture and transportation. Towards this application, technical hurdles remain because of the slow kinetics and strict operating conditions often associated with hydrates growth. Several promoters exist, which can affect thermodynamic and/or kinetic properties of clathrate hydrates. Stimulated by experiments that quantified the effect of L-tryptophan (TRP, a kinetic promoter) [1], we implemented atomistic molecular dynamics (MD) simulations to shed light on the molecular mechanisms responsible for hydrates growth in the presence of TRP. The simulations were conducted in the temperature range from 269.1 to 279.1 K, with excess CO₂ molecules and varying TRP concentrations. The results are quantified in terms of hydrate's growth rate, changes in hydrate cages and interpreted on the basis of density profiles, as well as by the free energy landscape relevant for the processes of interest. Our findings are in general agreement with experimental observations, as T=279.1 K is found to be the melting temperature for the CO₂ hydrate at the conditions considered for this study. A variety of phenomena are observed from the MD trajectory, including the adsorption of TRP molecules onto the hydrate surface. A number of analyses has been done to investigate the impacts of such adsorption behaviour, including metadynamics, mean-square displacement, density and residence time analysis. It has been discovered that the adsorption of TRP alters the kinetics and morphology of the hydrate system, and the growth rate of the hydrate slab is higher when TRP is adsorbed as compared to when TRP is far away from the hydrate-liquid interface. Combining our simulation results with experimental observations from the literature, we discuss a possible mechanism of how TRP kinetically promotes the growth of CO₂ hydrates. These insights could enable the future use of clathrate hydrates for CO₂ sequestration and transport.

[1] Khandelwal H, Qureshi MF, Zheng J, Venkataraman P, Barckholtz TA, Mhadeshwar AB, et al. Effect of L-tryptophan in promoting the kinetics of carbon dioxide hydrate formation. *Energy & Fuels*. 2020 Dec 24;35(1):649–58

Improvement of hydrogen clathrate formation by reverse micelles and optimization of the formulative parameters

Michele Ciulla^{1,*}, Serena Pilato¹, Gabriella Siani¹, Nadia Barbacane¹, Rafal Damian Wolicki¹, Claire Pirim², Bertrand Chazallon², Pietro Di Profio¹

¹ Department of Pharmacy, University "G. d'Annunzio" of Chieti-Pescara, via dei Vestini 31, 66010 Chieti, Italy.

² Univ. Lille, CNRS, UMR 8523 – PhLAM-Physique des Lasers Atomes et Molécules, CERLA – Centre d'Études et de Recherche Lasers et Applications, F-59000 Lille, France

*Corresponding author: M. Ciulla (michele.ciulla@unich.it)

The efficient storage of hydrogen is a critical enabling technology for its wider application in energy sectors, encompassing stationary and portable power generation, as well as transportation. Current methodologies for hydrogen storage, such as high-pressure compression (up to 70 MPa), liquefaction at cryogenic temperatures (20 K), and adsorption onto metal hydrides, all present significant drawbacks [1]. Clathrate hydrates, ice-like crystalline structures formed under moderate temperature and pressure conditions, offer a potentially transformative approach. These inclusion compounds feature a hydrogen-bonded network of water molecules that can encapsulate small guest molecules, including hydrogen, methane, and carbon dioxide. While their formation poses operational challenges in the oil and gas industry due to pipeline blockages, clathrate hydrates have gathered significant research interest for their potential in gas separation and storage/transportation applications.

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 [2]. 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, even for large-size aerospace installations [3].

The aim of this work falls within the PRIN 2022 PNRR project entitled “Low-cost, high-safety hydrogen storage into chemically-enhanced clathrate hydrates for energy storage in planetary infrastructures” (Brave New Worlds, CUP D53D2301693000, funded by the European Union – Next Generation EU) led by the University “G. d'Annunzio” of Chieti – Pescara, the University “Aldo Moro” of Bari, and the National Institute for Astrophysics of Catania as a research units.

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, and macroemulsions/binary systems.

Both in nano- and macro-systems, the THF concentration has been tuned in the range of stability of the clathrates at constant pressure of 10 MPa and temperature of 270 K, starting from its maximum amount and decreasing until the formation of clathrates ceased. We prepared different solutions of 80%, 60%, 40%, 30%, and 20% in THF with respect to the maximum stoichiometric concentration of 5.56% for the reverse micelles system; regarding the macroemulsion system, the THF was tuned at 13%, 16% and 19% in function of the partition coefficient between water and isoctane. We found that the kinetics of hydrate formation was enhanced, and also the amount of hydrogen enclathrated was increased as compared to the non-adjuvanted system. It was also observed that a value of 40% of THF is the minimal concentration to stabilize the formation of clathrates.

Bibliography

[1] Di Profio P, Arca S, Rossi F, Filipponi M. *Int J Hydrogen Energy* 2009;34:9173–80.

[2] Di Profio P, Arca S, Germani R, Savelli G. *J Fuel Cell Sci Technol* 2007;4:49–55.

[3] Di Profio P, Canale V, Germani R, Arca S, Fontana A. *J Colloid Interface Sci* 2018;516:224–31.

CCS - CO₂ hydrate formation kinetics in porous media under depleted reservoir storage conditions.

Peyman Dehghani^{1*}, Anh Minh Tang², Nicolas Gland¹, Eric Lecolier¹, Livio Ruffine¹,
 Anne Sinquin¹

¹ IFP Energies nouvelles, Rueil-Malmaison, France.

² Navier, Ecole des Ponts, Université Gustave Eiffel, CNRS, Marne-la-Vallée, France.

Large scale Carbon Dioxide (CO₂) storage in geological reservoirs (oil and gas reservoirs, deep saline aquifers, and coal seams mainly) offers a promising approach for addressing climate change by mitigating greenhouse gas emissions. In the case of depleted oil and gas reservoirs, the success of such a storage will depend on various factors among which the efficiency of CO₂ injection, particularly in the near-wellbore region where flow rates are high. In this area, pressure decrease close to adiabatic condition may lead to cooling Joule-Thomson effects and induces CO₂ hydrate formation. This hydrate formation can significantly reduce the injectivity and jeopardize well operations on-site.

This work aims at investigating the likelihood of CO₂ hydrates formation during CO₂ injection into depleted reservoirs and evaluating the related kinetics. The selected approach consists of undertaking laboratory experiments at two different and complementary scales: the pore scale by using microfluidic chip to investigate statistical occurrence of hydrate nucleation in numerous isolated CO₂ droplet/bubbles and the natural sediment analog, such as sand pack, to estimate the hydrates growth and distribution in porous media. The investigation specifically focuses on understanding the impact of different parameters, such as salinity and subcooling temperature. The pore-scale experiments employ the IFPEN® microfluidic platform to investigate the formation of CO₂ hydrates (liquid/gas) under pressure and temperature conditions relevant to the near-wellbore region during CO₂ storage in depleted reservoirs. CO₂ liquid droplets or gas bubbles are injected in a continuous water phase using a “Y-junction” microfluidic chip. These micron droplets or bubbles are then stored in a serpentine channel under pressure, with each isolated droplet serving as an isolated reactor. The generation of a large number of droplets facilitate the establishment of statistical laws governing hydrate nucleation and growth. The macroscale investigation of CO₂ hydrate formation kinetics within a sandy sediment (Fontainebleau silica sand) enables us to evaluate the hydrate distribution using X-ray scanning. The selected sand grains ranges in size from 140 to 320 microns. Employing the microfluidic method for monitoring crystallization over time, with estimating hydrate growth and distribution in porous media, could facilitate the development of a comprehensive kinetic law for CO₂ hydrate formation. The acquired knowledge and data are invaluable for understanding carbon storage in porous rocks within depleted hydrocarbon reservoirs.

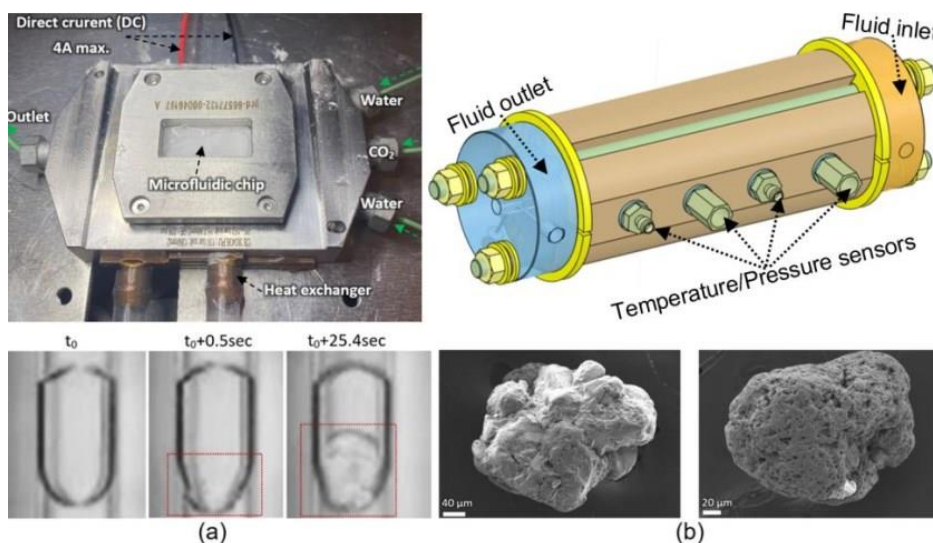


Figure 1. (a-up) Holder with a Y-junction/serpentine microchip (a-down) CO₂ liquid droplets in water/hydrate growth (b-up) Cell made of PEEK (b-down) Examples of Fontainebleau silica sand grains.

Partition of CO₂ into clathrate hydrate cages: investigation by vibrational spectroscopy

Rima Haidar^{1,2}, Carla, T. Rodriguez^{1,2}, C; Pirim^{1,2} and B. Chazallon^{1,2}

¹Univ. Lille, CNRS, UMR 8523 - PhLAM - Physique des Lasers Atomes et Molécules, F-59000 Lille, France, rima.haidar@univ-lille.fr, bertrand.chazallon@univ-lille.fr

²CERLA – Centre d'Études et de Recherches Lasers et Applications, F-59000 Lille, France

Gas hydrates are crystalline compounds formed from water and gas molecules under specific temperature and pressure conditions. They represent a huge potential for various applications, including energy storage [1] and CO₂ capture [2]. Their natural occurrences on Earth [3a] or possibly in the solar system [4], make them a credible option as natural endo- (Earth) and exogenous (Europa, Enceladus) gas and energy reserves [3b], and provides a better understanding of the formation history of these systems.

This research primarily focuses on the characterization of the formation process and storage capacity of gas hydrates, as well as the examination of the partition of CO₂ into clathrate cages. Binary and ternary mixtures forming simple or mixed gas hydrates were selected for (1) their relevance in a carbon capture context and (2) to highlight the specific partition of CO₂ into the cages of structure I: CO₂-H₂O, 20%CO₂+80%N₂-H₂O, 10%CO₂+80%N₂-H₂O, and 90%CO₂+10%C₃H₆. Vibrational spectroscopy (ex: FTIR) is used to analyze CO₂ signatures in the large and small cages, and retrieve CO₂ relative partitioning into the cages. The synthesis process involves a two-stage approach in which the ice particles are exposed to the gas or gas mixture under controlled conditions of temperature (-3°C or 3°C) and pressure (25-120 bar). In addition, the kinetics of gas hydrate formation are studied through volumetric measurements and experiments involving vapor deposited ice as starting material with different levels of compaction. Gas absorption calculations are performed to determine the rate of hydrate formation and gas storage capacity. This comprehensive approach provides a better understanding of the structure, composition and kinetics of CO₂-based gas hydrates. It will help to improve the development of hydrate-based technologies and gas storage methodologies.

[1] Farrando-Perez et al., *Nature* (2022) 13:5953

[2] Chazallon & Pirim, *Chem Eng Sci.* (2018), 342, 171-183

[3a] Chazallon et al., *Marine & Petroleum Geol.* (2021) 124, 104785 ;[3]b Boswell et al., (2020) In *Natural Gas Hydrates: Status of Potential as an Energy Resource*, Future Energy, 108-130

[4] Villanueva et al., *Science*, (2023) 381, 1305-1308 ; Shibley & Laughlin, *Planet. Sci. J.*, (2021) 2:221

Rheological characterization of various mixtures of CO₂ hydrate slurries for low temperature refrigeration applications

Rihab Khirallah^{*1}, Yasmine Salehy¹, Sébastien Saavedra¹, Pascal Clain^{1,2}, Véronique Osswald¹,
Hong-Minh Hoang¹, Laurence Fournaison¹, Anthony Delahaye¹

¹*Université Paris-Saclay, INRAE, FRISE, 92761, Antony, France*

²*Léonard de Vinci Pôle Universitaire, Research Center, 92916 Paris la Défense, France*

In secondary refrigeration, CO₂ hydrate slurries act as a phase-change material, which could help reducing primary refrigerant amounts. Hydrates absorb heat during their formation and release it during their dissociation. This property makes them effective in maintaining low temperatures, and allow the reduction of temperature variation across heat exchangers, which improves energy efficiency of the cooling system. In addition, CO₂ hydrate slurries used as a secondary refrigerant is favored for its environmental friendliness as it has low global warming potential compared to some traditional refrigerants used for direct refrigeration.

Recent work focusing on industrial performance assessment showed that CO₂ hydrate slurries could be suitable for air-conditioning. But for refrigeration application dedicated to food preservation, hydrate slurries should be stable at lower temperature. The present paper aims at understanding the operational conditions for using hydrate slurries in such application, namely temperature stability and flowing properties. In particular, characterizing the rheology of hydrate slurries is crucial to understand their behavior during cold transport and optimizing pumping power. Thus, we focused on the rheological characterization of CO₂ hydrate slurries in a dynamic loop using the Osswald viscometer, in order to study parameters such as the behavior index, consistency index, and shear stress throughout hydrate formation. Various mixtures to form hydrates were tested, with or without additives (ethanol, surfactant...), in order to vary the set point temperature and pumping power. The results showed that the viscosity of the various CO₂ hydrate slurries increases with the decrease of the shear rate, exhibiting a shear-thinning behavior. These rheological properties were used to simulate the overall performances (energy efficiency, cost) of the system.

Optimizing the formation of hydrates for highly efficient CO₂ capture

Doyeon /Kim¹, Jeong-Hoon /Sa²

¹ Department of Chemical Engineering, Dong-A University, Busan, South Korea,
1929914@donga.ac.kr

² Department of Chemical Engineering, Dong-A University, Busan, South Korea, jhsa@dau.ac.kr

Carbon capture, utilization and storage (CCUS) has gained significant attention as a crucial component of global efforts to address climate change. CO₂ emissions from industrial processes constitute approximately 40% of the total CO₂ emissions, making it one of the major contributors to the greenhouse effect. An effective capture and separation of CO₂ is thus essential to achieve carbon neutrality. Currently employed absorption, adsorption, and membrane separation technologies still suffer from high energy consumption, low efficiency, and complexity in process maintenance and management. Clathrate hydrate, a crystalline solid compound formed by hydrogen-bonded water frameworks capturing gas molecules under appropriate thermodynamic conditions, holds significant potential for CO₂ capture. Despite extensive efforts, hydrate-based gas separation technologies have not yet been realized due to their insufficient gas separation efficiency. Clathrate hydrates are generally classified into three structures: structure I (sI, Pm3n), structure II (sII, Fd3m), and structure H (sH, P6/mmm). In previous studies, thermodynamic hydrate promoters (THPs) such as tetrahydrofuran (THF) and cyclopentane have been used to induce hydrate formation under mild conditions. However, THPs occupy the large cages of sII hydrates by themselves, resulting in unavoidable reduction in gas storage capacity. In addition, a competition between H₂ and CO₂ molecules in occupying the remaining small cages of sII hydrates resulted in the limited CO₂ purity. Conversely, if one can utilize the sI hydrates, which have 6 large cages and 2 small cages per unit cell, it is more likely to increase the CO₂ purity. However, formation of sI CO₂ + H₂ hydrates still requires higher pressure conditions, and thus it is challenging to achieve high gas storage capacity in hydrates. In this study, we developed a new process intentionally utilizing the formation of CO₂ (40%) + H₂ (60%) sI hydrates instead of using a stoichiometric concentration of THF (5.56 mol%) for sII hydrate formation. We employed a fixed-bed reactor filled with hydrophobically modified silica sand and introduced a small amount of THF for a rapid formation of sII hydrates, acting as a seed to induce sequential sI hydrate formation. This strategy would significantly reduce the induction time, which is often a major drawback of the hydrate-based processes. The concentration of THF was varied (0.3, 0.5, and 1 mol%) to optimize this new strategy. The changes in gas phase composition was monitored by using an in-situ gas chromatography, and CO₂ composition in hydrate phase was estimated by the mass balance calculation. According to the results, the use of hydrophobically modified silica sand was more effective to achieve a high separation efficiency over the raw sand. These findings would demonstrate the innovative improvement of hydrate formation kinetics and the achievement of a highly efficient CO₂ separation process suitable for large-scale CO₂ capture and separation applications.

On the use of Gas Hydrates by a CO₂-based Electrothermal Energy Storage System: Modeling and Evaluation

A.-S. Kyriakides¹, A. Stoikos^{1,2}, D. Trigkas^{1,3}, G. Gravanis^{1,4}, S. Voutetakis¹,
I.N. Tsimpanogiannis¹

¹ *Chemical Process & Energy Resources Institute (C.P.E.R.I.), Centre for Research and Technology Hellas (CE.R.T.H.), P.O. Box 60361, 57001, Thessaloniki, Greece*

² *Department of Mechanical Engineering, Aristotle University of Thessaloniki, 54124, Thessaloniki, Greece*

³ *Department of Industrial Engineering and Management, International Hellenic University, 57001, Thessaloniki, Greece*

⁴ *Department of Information and Electronic Engineering, International Hellenic University, 57001, Thessaloniki, Greece*

i.n.tsimpanogiannis@certh.gr

In order to reduce the energy dependency on fossil fuels of our society it is essential to develop innovative solutions for energy storage that will enable us to further increase the use of renewable energy sources. Among those solutions suggested in the literature, the case of electrothermal energy storage appears to be very promising. The particular solution consists of a heat pump (charge cycle) and a heat engine (discharge cycle) using transcritical CO₂ cycles, water as a thermal energy storage fluid to store sensible heat, and ice as a cold storage medium to store latent heat.

During the charge cycle, surplus renewable electricity is converted to heat and is stored as sensible and latent heat. Subsequently, this heat is converted, during the discharge cycle, to electricity during peak demand hours, thus partially recovering the stored energy. The use of CO₂ as a working medium is adequate for these energy conversion processes in the temperature range of this application as CO₂ is stable throughout the entire temperature range of operation, can easily cross the CO₂ critical point, has good thermal properties, is nontoxic, nonflammable, and environmentally friendly.

Such a system was examined systematically in a recent study [1]. By performing a parametric sensitivity analysis, the study evaluated the system's performance under conditions of progressively lower freezing points. It was concluded that the round-trip efficiencies of the process increased as the freezing points of the cold storage medium increased. Motivated by the aforementioned observation, in the current study, we examine further cases of cold storage mediums with freezing points that are higher than the cases of ice slurries considered in the recent study. Excellent candidates with such behavior are the cases of gas hydrates or semiclathrates. We also explore the possibility of using aspects of hydrate science and technology in other parts of the proposed energy storage system.

References

[1] Kyriakides et al., *Chem. Eng. Trans.* **103**, 505-510, 2023.

Acknowledgements

This research has received funding from the European Union HORIZON Europe project CEEGS-NOVEL CO₂-BASED ELECTROTHERMAL ENERGY AND GEOLOGICAL STORAGE SYSTEM, under Grand Agreement Number: 101084376.

Phase equilibria and formation kinetics of CF₃I hydrates as clean fire extinguishing agents

Jonghwan/Lee¹, Yebom/Shin², Sang-Gyu /Cho³, Jeong-Hoon/Sa⁴

¹ Department of Chemical Engineering, Dong-A University, Busan, South

Korea, jhwanlee10@gmail.com

² Department of Chemical Engineering, Dong-A University, Busan, South Korea, suyk01@naver.com

³ Offshore Plant Resources R&D Center, Korea Institute of Industrial Technology, Busan, South

Korea, sgcho96@kitech.re.kr

⁴ Department of Chemical Engineering, Dong-A University, Busan, South Korea, jhsa@dau.ac.kr

As the large-scale forest fires and high-rise building fires have often occurred in recent days, a new type of fire extinguishing agents that can be used for such events is required. Gas hydrate-based fire extinguishing agents can effectively suppress fires by cooling and/or smothering. Gas hydrate-based fire extinguishing agents can be actively suppressed because they can be thrown at high floors from a long distance. It is also a clean fire extinguishing agent that does not leave any residual pollutants when a fire is extinguished because it is composed of water. In a previous study, research was conducted on extinguishing agents using CO₂ hydrate, and it was shown to extinguish fire more effectively than ice or dry ice. In addition, research on the basic properties of gas hydrates using HFC-23 and HFC-125, which can be used as fire extinguishing agents, was also conducted. Despite previous studies, hydrate-based fire extinguishing agents have not yet been commercialized. In this study, we investigated the thermodynamic and kinetic properties of CF₃I hydrate as CF₃I (trifluoroiodomethane) has a great potential as a fire extinguishing agent due to its near zero ozone depletion potential and low greenhouse warming potential (0.4). Based on the x-ray diffraction data, CF₃I was found to occupy large cages of structure II hydrates. According to the phase equilibrium measurement of CF₃I hydrates in the range of (279.35~284K, 1.0~3.5bar), CF₃I hydrates can form at relatively mild conditions compared to other HFC-23, HFC-125 etc.) hydrates, and they can even form at 279.35K under atmospheric pressure. When NaCl was added, the phase equilibria shifted to the lower temperature and higher pressure regions. Hydrate formation temperature in the presence of 3.5wt% and 8.0 wt% NaCl solution shifted 1.7 K and 3.7 K, respectively. The reliability of phase equilibrium data was checked by using the HLS (Hu-Lee-Sum) correlation. According to the kinetics measurements, while the formation rate and water to hydrate conversion of CF₃I hydrate were quite low, the use of 3000 ppm L-tryptophan (L-trp) or sodium dodecyl sulfate (SDS) as kinetic promoters significantly increased the formation rate and conversion (~100%). In particular, L-trp is environmentally friendly and thus preferred as a kinetic promoter. Our experimental results demonstrate that CF₃I hydrates have a great promise for fire extinguishing applications. In addition, it can also be implied that CF₃I can potentially be used as thermodynamic promoter for hydrate-based clean energy storage applications.

Experimental and Computational Investigation on Multiphase Flow Behavior of CO₂ injection into Deep-Sea Sediment

Yohan Lee^{1,2}, Jonghyuk Lee², Woojin Go³, Yongwon Seo², Arnaud Desmedt^{1,4}

¹ Institut des Sciences Moléculaires, Bordeaux, France, yohan.lee@u-bordeaux.fr

² Ulsan National Institute of Science & Technology, Ulsan, Republic of Korea ³

Seoul National University, Seoul, Republic of Korea ⁴

Laboratoire Léon Brillouin, Saclay, France

Sub-seabed geological CO₂ storage has high gas storage capacity and long-term storage stability, which has attracted extensive research interest in the field of greenhouse gas (GHG) reduction. However, the impact of CO₂ hydrates on multiphase flow behavior during injection is not well understood. Due to the favorable environment for hydrate formation in deep-sea sediments, CO₂ injection could cause severe hydrate formation near the injection well. To optimize the CO₂ injection process concerning potential hydrate plugging, it is essential to investigate the flow behavior and distribution of multiphase fluids, including water, liquid CO₂, and CO₂ hydrates. In this study, a specially designed one-dimensional (1-D) reactor was used to monitor pressure changes at 274.2 K during liquid CO₂ injection at a pressure of 65 bar. A rapid increase in pressure was observed about 1 hour from the start of injection, and the pressure reached the shutoff pressure (120 bar) at about 2 hours. The flow rate at the outlet gradually decreased, and intermittent hydrate plugging was also observed. To visualize the invisible processes during injection, Computational Fluid Dynamics (CFD) simulations were performed using OpenFOAM. The CFD simulations employed a volume of fluid (VOF) method to handle complex interface dynamics and to model the surface tension of multiphase fluids. The hydrate formation and growth kinetics as well as the transport properties of the hydrate phase were determined based on previous literature and rheological analysis. The CFD simulations, combined with experimental results, provide predictions of hydrate plugging (spatially, temporally, and quantitatively) and highlight the importance of reliable hydrate induction time and transport properties of hydrates. Overall, this study provides further understanding of complex multiphase flow phenomena considering hydrate formation and its distribution during CO₂ injection in deep-sea sediments. Additionally, the results offer insights into better management strategies for hydrate formation near the injection well.

Ultra-rapid CO₂ hydrate formation kinetics enabled by magnesium coupled with amino acid as promoter

Yan Li¹, Zhenyuan Yin¹, Xuejian Liu¹, ...

¹ Institute for Ocean Engineering, Shenzhen International Graduate School, Tsinghua University, Shenzhen 518055, China

In this study, we systematically investigated an environmental-benign kinetic promoter (*L*-leucine, *L*-Leu) coupling magnesium to enhance CO₂ hydrate formation at the pressure of 3.5 MPa and temperature of 275.2 K. The results showed that CO₂ hydrate did not form in pure water for 7 days despite the *P* and *T* conditions within the equilibrium region. The induction time (t_{ind}) of CO₂ hydrate was reduced to 696.65 minutes in the addition of 1.0 wt% *L*-leu. When magnesium was introduced to enhance CO₂ hydrate formation, it showed a superior promotion effect on reducing t_{ind} to less than 10 s. In pure water, the dense CO₂ hydrate film at the gas-liquid interface blocked the mass transfer and the CO₂ gas uptake was 10.44 V^g/V^w. Therefore, magnesium was applied to trig CO₂ hydrate nucleation coupling *L*-leu to realize rapid CO₂ hydrate formation, followed by rapid *P* drop with the CO₂ gas uptake of 78.77 V^g/V^w (see Fig. 1a). In the coupling system, CO₂ hydrate formation rate was promoted effectively with the t_{90} of 85.08 min under the static condition (see Fig. 1b). Superior CO₂ gas uptake of 129.42 V^g/V^w can be achieved at higher gas-liquid ration of 8.06. Fig. 1c-h depicts the morphology of CO₂ hydrate formation process in the coupling system. CO₂ hydrate nucleation was triggered by Mg plate at the gas-liquid interface and the snow-like CO₂ hydrate growth along the wall was observed. When coupled with other hydrophobic amino acids, such as *L*-met, *L*-trp, CO₂ gas uptake over 130.00 V^g/V^w can be obtained. However, when coupled with hydrophilic amino acid such as *L*-arg, t_{ind} was induced but only limited CO₂ uptake (21.77 V^g/V^w).

This work provides an insight into the promotion effect of coupling magnesium and amino acid on CO₂ hydrate nucleation and growth processes, combined with the morphological investigation. And it also contributes to offering considerable enhancement in the kinetic process of CO₂ hydrate formation, which can be utilized for various hydrate-based technologies such as CO₂ sequestration.

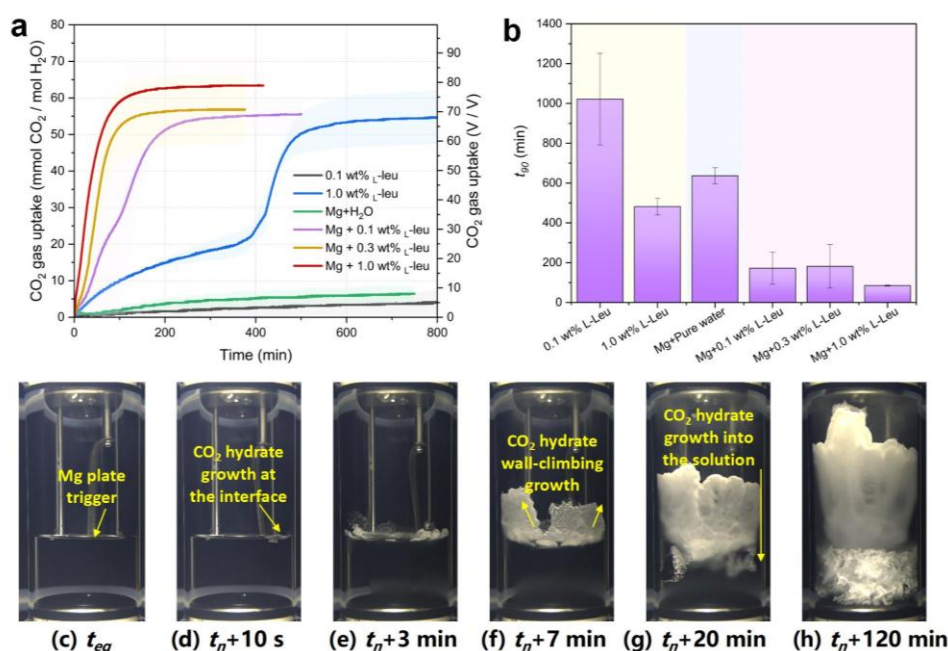


Fig.1 (a) Normalized CO₂ gas uptake profiles during CO₂ hydrate formation with and without Mg plate trigger for *L*-leu concentrations varying from 0.10-1.00 wt% at *T* = 275.2 K and *P*₀ = 5.5 MPa in the static system.(b) Comparison of t_{90} (time required to achieve 90% CO₂ final gas uptake in hydrate).(c-h) Morphological evolution during CO₂ hydrate formation triggered by Mg plate in 1.00 wt% *L*-leu.

A Novel Method for Natural Gas Hydrate Production: Depressurization and Backfilling with In-situ Supplemental Heat

Yuxuan Li¹, Shouding Li^{1*}, Zhaobin Zhang¹, Xiao Li¹

¹ *Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, China*

Corresponding author : Shouding Li, Email : lsdlyh@mail.iggcas.ac.cn

Natural gas hydrate resources are abundant and are recognized as the most promising new type of efficient and clean alternative energy, representing a strategic breakthrough for future energy revolution. However, the safe and economical exploitation of natural gas hydrates still faces numerous bottlenecks due to the complex physical and chemical processes accompanying hydrate decomposition. Currently, depressurization is a relatively economically effective extraction method, but the average daily production of natural gas falls far short of the demands for industrial development.

Based on an analysis of the bottleneck issues faced by the scale-up of depressurization, a novel method for the extraction of natural gas hydrates is proposed - the in-situ reheating and depressurization filling method using calcium oxide-based composite materials. This method involves injecting calcium oxide-based coating materials into natural gas hydrate reservoirs, where these materials react with water in the reservoir over a certain period, releasing a large amount of heat. This process sufficiently supplements the heat required for the decomposition of natural gas hydrates. Additionally, the solid calcium hydroxide generated from the reaction between the calcium oxide-based materials and water expands in volume, increasing porosity, which not only fills the voids left after the decomposition of natural gas hydrates but also enhances reservoir permeability.

We conducted indoor experiments, numerical simulations, and field-scale tests in the Qilian Mountain permafrost region to fully verify the feasibility of reservoir temperature field transformation methods and the in-situ reheating and depressurization filling extraction theory. This breakthrough not only lays a solid foundation for establishing mechanisms for the evolution of temperature and pressure fields and flow assurance in natural gas hydrate pilot production systems but also provides crucial support for refining optimization models for the permeability of different types of natural gas hydrate reservoirs in various marine environments. Moreover, it offers important insights for the development of new methods for the commercial extraction of natural gas hydrates in the future.

Clathrate hydrates: A cool way to store carbon dioxide permanently.

Praveen Linga

Department of Chemical and Biomolecular Engineering, College of Design and Engineering, National University of Singapore, Singapore

Climate change is known to be dominantly caused by the increased concentration of greenhouse gases in the atmosphere, in particular carbon dioxide (CO₂). The clathrate hydrate process has been demonstrated over the years as promising technology for innovative applications like natural gas storage, carbon dioxide capture, seawater desalination, cold energy storage etc. CO₂ hydrate, a solid compound made of molecular CO₂ enclathrated in crystalline lattices formed by water molecules, is an attractive option to capture and for long-term CO₂ sequestration. Methane (CH₄) hydrates in oceanic sediments have been stable for millions of years. As a natural analog, is it possible to store CO₂ in the form of hydrates in oceanic sediments forever? In this presentation, the state of the art on clathrate hydrate technology pertaining to carbon capture and storage will be discussed in detail. Furthermore, future research and development opportunities and pathways for commercialization will be discussed.

Molecular simulations of mixed clathrate hydrates including ionic species

Victoire Meko Fotso¹, Arnaud Desmedt^{2,3}, Sylvain Picaud¹, Ludovic Martin-Gondre¹

¹Institut UTINAM, UMR6213 CNRS – Univ. Franche-Comté, Besançon, France

²Institut des Sciences Moléculaires (ISM), UMR5255 CNRS – Univ. Bordeaux, France

³Laboratoire Léon Brillouin (LLB), UMR12 CEA-CNRS - Univ. Paris-Saclay, France

The world faces a dual challenge of climate change driven by greenhouse gas emissions and the finite nature of fossil fuels. Hydrogen turns out to be an alternative to solve this problem since its combustion leads to water and energy. However, hydrogen storage and safe transportation remains a challenging task. Among all proposed hydrogen storage materials, storage in clathrate hydrates constitutes an attractive hosting environment [1]. In this work, we initially studied the properties of neutral systems presenting interesting characteristics for hydrogen storage: N₂ gas hydrate for its storage capacity and Xe gas hydrate for its thermodynamic stability in soft conditions. In addition, a second promoter is considered in order to improve the H₂ diffusion. Indeed, ionic species (such as HClO₄) can modify the dynamics properties of the aqueous network and help the H₂ inter-cage diffusion [2]. The properties of mixed clathrate hydrates are determined by Density Functional Theory (DFT) simulations using the Vienna Ab initio Simulation Package (VASP) and considering two functionals. Initially, the structural properties of mixed hydrates are studied. Then, the thermodynamic properties of clathrates are evaluated with a convex hull approach in order to extract effects of pressure and acid composition on stability.

[1] Gupta A., Baron G.V., Perreault P., Lenaerts S., Ciocarlan R-G, Cool P., Mileo P.G.M., Rogge S., Van Speybroeck V., Watson G., Van der Voort P., Houlléberghs M., Breynaert E., Martens J., Denayer J.F.M., **2021**. Hydrogen Clathrates: Next Generation Hydrogen Storage Materials. *Energy Storage Mat.* 41, 69-107.

[2] Nguyen T.T., Petuya C., Talaga D., Desmedt A., **2020**. Promoting the Insertion of Molecular Hydrogen in Tetrahydrofuran Hydrate With the Help of Acidic Additives. *Frontiers in Chemistry* 8, 550862.

Hydrate-based gas separation of systems including hydrogen in porous media: A thermodynamic approach

Saheb Maghsoodloo¹, Nicolas Ferrando¹

¹ IFP Energies Nouvelles, 1 et 4 Avenue de Bois-Préau, 92852 Rueil-Malmaison Cedex, France

Hydrogen separation/purification is a potential application of gas hydrates. A remarkable feature of hydrate crystallization process is that guest composition in hydrate phase is different from feed, leading to a selective component distribution in gas and hydrate phases. The design parameters of hydrate-based hydrogen separation process can be improved by crystallization in porous media instead of in bulk phase. In fact, that the formation rate increases in the porous media due to the improvement of gas-liquid contact area [1]. Moreover, the guest enclathration in the solid phase could be modified in confined systems.

In this study, a thermodynamic framework has been developed to predict the thermodynamic equilibrium of systems including hydrogen in confined environment. The approach is based on van der Waals and Platteeuw method for hydrate phase and CPA equation of state for the fluid phases. The capillary effect generated by pores has also been taken into account since it decreases the activity of water [2,3]. The framework allows to determine the number of ideal equilibrium stages for separation process. In addition, the maximum temperature (or minimum pressure) required for the separation/stockage can be predicted.

In order to predict correctly the hydrate equilibrium behavior of H₂ in presence of CO₂, CH₄, C₂H₄, C₃H₈, the binary parameters of CPA have been fitted to VLE experimental data. Moreover, parameters of solid model have been regressed with hydrate dissociation equilibrium data.

Then, separation strategies have been studied and discussed on PTxy diagrams (Pressure-Temperature-Hydrate-Vapor compositions) of a case study CO₂/H₂ system in porous media. The results showed that a given feed composition, a very rich-CO₂ solid phase (spec: 99 mol% CO₂) could be obtained by a two-stage hydrate-base equilibrium process and by optimizing temperature/pressure conditions. The CO₂ recovery in hydrate phase can be augmented from 36 to 70% by decreasing the operational temperature from 277.15 to 271.15 K. Below this temperature, the CO₂-recovery does not change significantly. However, to recover a H₂-rich vapor phase (spec: 94 mol% H₂) lower temperature is required. In fact, it was remarked that the hydrogen specification can be reached only at temperatures lower than 250.15 K. Furthermore, the calculations revealed that the separation can be improved if multi-stage equilibrium at different temperatures is used. The optimized design leads to recover 91 and 82 % of H₂ and CO₂, respectively.

References

- [1] N. Gholipour Zanjani et al., Journal of Petroleum Science and Engineering 96-97 (2012) 102–108.
- [2] J.W. Wilder et al., Langmuir 17 (2001) 6729–6735.
- [3] M.A. Clarke et al., Ind. Eng. Chem. Res. 38 (1999) 2485–2490.

Molecular insights into hybrid CH₄ physisorption-hydrate formation in spiral halloysite nanotubes: Implications for energy storage

Fengyi Mi^{1,2}, Zhongjin He^{*1}, Jiangtao Pang¹, Othonas A. Moutos², Thijs J.H. Vlugt²,
Guosheng Jiang¹, Fulong Ning¹

¹ National Center for International Research on Deep Earth Drilling and Resource Development, Faculty of Engineering, China University of Geosciences, Wuhan, Hubei 430074, China

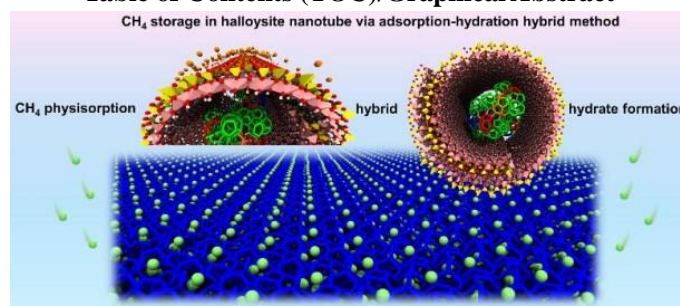
² Engineering Thermodynamics, Process & Energy Department, Faculty of Mechanical Engineering, Delft University of Technology, Leeghwaterstraat 39, Delft, 2628CB, the Netherlands

*Authors to whom correspondence should be addressed. hezhongjin@cug.edu.cn

Abstract: A microscopic insight into hybrid CH₄ physisorption-hydrate formation in halloysite nanotubes (HNTs) is vital for understanding the solidification storage of natural gas in the HNT and developing energy storage technology. Herein, microsecond large-scale classical molecular dynamics simulations are conducted to investigate CH₄ storage in the HNT via the adsorption-hydration hybrid method and to reveal the effect of the gas-water ratio. The simulation results indicate that the HNTs are excellent nanomaterials for CH₄ storage via the adsorption-hydration hybrid method. CH₄ physisorption and hydrate formation inside and outside of the HNTs are profoundly influenced by the surface properties of the HNTs and the kinetic characteristics of CH₄/H₂O molecules. The outer surfaces of the HNTs exhibit relative hydrophobicity and adsorb CH₄ molecules to form surface nanobubbles, moreover, CH₄ molecules adsorbed on the outer surface are tightly trapped between the hydrate solids and the outer surface, inhibiting their kinetic behavior and favoring CH₄ storage via physisorption. The inner surface of the HNTs exhibits extreme hydrophilicity and strongly adsorbs H₂O molecules, thus, CH₄ hydrate can form inside of the HNTs. It is more difficult for CH₄ and H₂O molecules inside of the HNTs to convert into hydrates than those outside of the HNTs. A moderate gas-water ratio is advantageous for CH₄ physisorption and hydrate formation, whereas excessively high or low gas-water ratios are unfavorable for efficient CH₄ storage. These insights can help to develop efficient CH₄ solidification storage technology.

Keywords: Methane storage; Halloysite Nanotube; Molecular dynamics simulation; Physisorption; Hydrate formation; Methane hydrate; Surface property.

Table of Contents (TOC)/Graphical Abstract



Geological CO₂ storage in subsurface tested in microfluidics coupled with microscope and Raman spectroscopy

Qian Ouyang¹, Jyoti Shanker Pandey¹, Nicolas von Solms^{1*}

¹ Center for Energy Resources Engineering (CERE), Department of Chemical Engineering, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark. nvs@kt.dtu.dk (N.v.Solms)

CO₂ hydrates are cage-like solid compounds consisting of CO₂ gas molecules and water molecules. The properties of CO₂ hydrates, such as high gas storage capacity and moderate formation conditions of pressure-temperature, are desirable for long-term geological CO₂ storage. The purpose of this work is to provide evidence of CO₂ hydrate formation in a microfluidic chip, and assess the safety and capacity of CO₂ storage in marine subsurface. While the microscopic morphologies of CO₂ in liquid and hydrate phases are similar, Raman spectroscopy is employed to distinguish CO₂ in phases of gas, water and hydrate.

Two scenarios in a hydrophilic chip were investigated regarding different CO₂ states controlled by different pressures above or below CO₂ liquid liquefaction pressure (PL-CO₂). In one scenario, the system pressures were kept lower than PL-CO₂ to form CO₂ hydrate. A pressure difference was observed in the system indicating hydrate blockage prevented unwanted CO₂ flow for safe CO₂ storage. In another scenario, the system pressures were increased over PL-CO₂, which was the typical marine subsurface pressure, to observe CO₂ hydrate formation in a system containing liquid CO₂. The differences in morphological patterns and Raman peak shifts were observed, verifying CO₂ could be stored in states of both hydrate and liquid. The quantitative CO₂ storage capacity showed about 80 volumes of CO₂ was retained in the system having only CO₂ hydrates, compared with about 150 volumes of CO₂ stored in the system having both CO₂ hydrates and liquid CO₂.

The morphological patterns, Raman spectra, hydrate-inducing blockage and storage capacity indicate that CO₂ hydrate could serve as a safe sealing and secondary storage option while liquid CO₂ as the main body for subsurface CO₂ storage. The results of this work are beneficial to understanding geological CO₂ storage in the confined space, and the enhanced CO₂ hydrate storage capacity can be explored by coupling with hydrate promotors and thus achieve more efficient CO₂ storage in marine subsurface conditions.

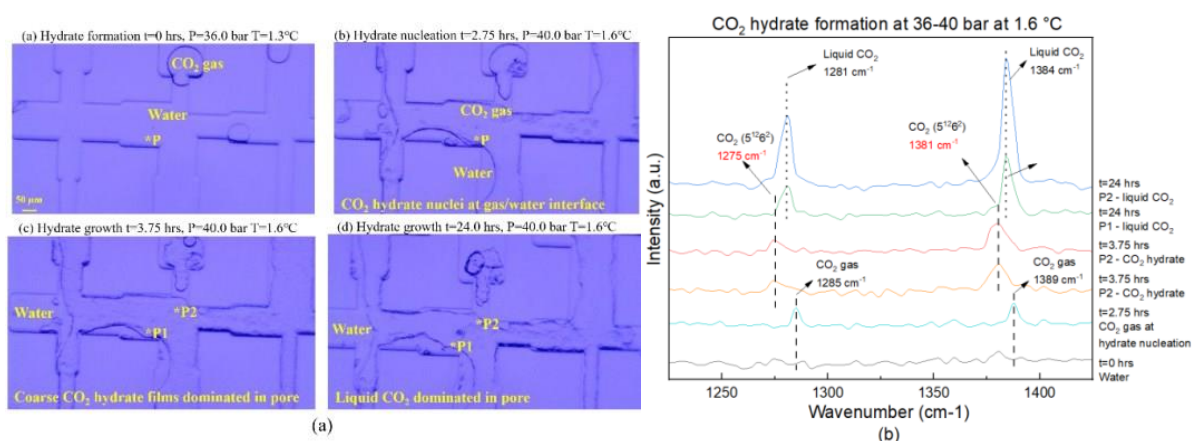


Figure 1. CO₂ hydrate formation in a hydrophilic chip under 36-40bar, 1.6°C with time-dependent: (a) morphologies of CO₂ in gas/water/hydrate/liquid. (b) Raman peaks of CO₂ in gas/water/hydrate/liquid.

Energy and Economic Analysis on Different Technologies of Natural Gas Storage

Beatrice Castellani¹, Ahmed OMRAN^{2*}, Valentin VALTCHEV^{2,*}

¹*Department of Engineering, CIRIAF, University of Perugia, Perugia, Italy*

²*Normandie Université, ENSICAEN, UNICAEN, Laboratoire Catalyse et Spectrochimie (LCS), 14050, Caen, France*

This study compares methane storage technologies based on energy consumption, density, costs, and safety for Solidified Natural Gas (SNG) via hydrates, Underground Natural Gas Storage (UNGS) [1], Compressed Natural Gas (CNG), and Liquefied Natural Gas (LNG), [2]. Thus, it aims to identify the most viable and efficient storage method through theoretical analysis, literature data mining, and experimental studies. The focus is on understanding each technology's specific requirements and economic implications to promote future energy storage decisions. The results highlight distinct differences across methane storage technologies. SNG's energy consumption ranges from 2115 to 2410 kJ/kgCH₄, with a primary energy content of 0.096-0.110 kJ/kJ, reflecting higher energy needs due to hydrate cooling processes. Conversely, CNG is the most energy-efficient, with the lowest consumption at 1321.8 kJ/kgCH₄. UNGS and LNG fall in the middle, with LNG having the highest energy density but also the highest costs. SNG's costs are competitive, indicating economic viability under certain conditions. Experimental data shows that 10 MPa and 275 K formation conditions are yielding sl methane hydrate with a 170-172 V/V uptake, matching theoretical predictions. Additionally, the storage at pressure 5-7 bar and 253 K for six months shows minimal methane loss, highlighting SNG's safe and efficient storage potential without needing compression in the storage phase.

CNG stands out as the most energy-efficient and initially cost-effective methane storage technology but faces high capital costs. Alternatively, SNG offers notable safety and environmental benefits, emerging as a strong contender. The selection of a storage method depends on specific project requirements, including geographical and safety factors. Advancements in lowering SNG's production and storage pressures and leveraging self-preservation could make it a more viable and sustainable option. Moreover, integrating SNG with CNG or LNG could provide a comprehensive solution that harnesses the strengths of each technology, presenting a unified approach to methane storage.

(1) Diamantakis *et al.* (2024). A review of analogue case studies relevant to large-scale underground hydrogen storage. *Energy Reports*, 11, 2374-2400.

(2) Economides, M. J., Sun, K., & Subero, G. (2006). Compressed natural gas (CNG): an alternative to liquefied natural gas (LNG). *SPE Production & Operations*, 21(02), 318-324.

CO₂ hydrates crystallization kinetic parametric study: effect of impeller type

Véronique OSSWALD¹, Pascal CLAIN^{1,2}, Didier DALMAZZONE³,
Anthony DELAHAYE¹, Laurence FOURNAISON¹

¹ Université Paris-Saclay, INRAE, FRISE, Antony, 92761, France, veronique.osswald@inrae.fr²
Léonard de Vinci Pôle Universitaire, Research Center, Paris la Défense, 92916, France³
ENSTA-Paris, UCP, Palaiseau 91120, France

CO₂ hydrate slurry is a promising phase change material for cold storage and 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. The goal here, for cooling application, is to increase the rate of CO₂ hydrate formation. Most laboratory-scale hydrate reactors are equipped with pressure and temperature probes, and mass balance on CO₂ allows formation kinetic studies, but with assumptions on CO₂ concentration in the liquid phase and the hydration number.

The present work investigates the kinetics of CO₂ hydrate crystallization for two different types of stirrers, on one hand a three pitched blade stirrer and on the other hand a hollow shaft eight blade Rushton turbine. We use a jacketed stirred batch reactor, with a specially developed sensor (a thermopile) to determine experimentally heat balance on the cooling jacket. The mass fraction of crystallized hydrate during the time is determined directly from this heat balance. Those results are compared with mass balance approach. To highlight the effect of stirrer type on mass transfer, especially between vapour and liquid phases, an additional experimental study to determine vapour/liquid mass transfer coefficient, $k_{L,a}$, were achieved. We conclude about the global performance for heat and mass transfers of both stirrer, and give general recommendation for the choice of stirrer type and scale-up process.

Hydrogen storage in C₂ hydrogen hydrate

Tomasz Poręba¹, Leon Andriambarijaona², M. Rescigno^{1,3}, R. Gaal¹, Livia Bove^{1,2,3}

¹ *Laboratory of Quantum Magnetism, Institute of Physics, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland, e-mail : tomasz.poreba@epfl.ch*

² *Sorbonne Université, UMR CNRS 7590, Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, 75252 Paris, France*

³ *Dipartimento di Fisica, Università di Roma La Sapienza, 00185 Roma, Italy*

Hydrogen hydrates are promising functional materials for clean energy storage and offer alternative to the current cryo-compressed hydrogen storage technology, insuring low production and operational costs, environmentally benign nature, and lower risk of flammability. Hydrogen hydrate clathrate sII phase transitions into the so-called “filled ice” forms above 1 GPa. In filled ice, the water frame assumes one of the known ice phases, and hydrogen occupies definite positions in the ice channels. Up to ~3 GPa, five different phases have been reported (C₋₁, C₀, C₁, C₁['], and C₂ respectively), with increasing hydrogen-to-water ratio [1-2]. Recently, a new C₃ phase with a hydrogen-to-water ratio of 2:1 [2] forming above 40 GPa, upon laser heating (~1200 K), and being stable up to 90 GPa, has also been observed.

It has been shown that the C₂-form of hydrogen hydrate (H₂O·H₂/ D₂O·D₂), which is constituted by an ice Ic skeleton, transforms into pure cubic ice Ic releasing molecular hydrogen upon decompression at 100 K [3]. However, the mechanism and kinetics of C₂ hydrogen loss is not well-defined. It was suggested to progress through sample amorphization, though no evidence of an amorphous intermediate state was observed by neutron diffraction. We have recently determined, *via* high-pressure neutron powder diffraction experiments, that the unit cell volume of the C₂ phase- produced in a Paris-Edinburgh (PE) cell at 3 GPa, and then recovered at ambient pressure and 78 K - continuously decreases upon heating above 100 K at ambient pressure. This indicates, at least partial, controlled hydrogen release without loss of crystallinity up to 130 K and the capability of C₂ to store hydrogen up to 100 K at ambient pressure.

Additionally, we present insights into structural deformation, hydrogen content and mechanisms of formation of C₂ under extreme p conditions [4].

[1] Ranieri, U. et al. *PNAS*, 120, 52 (2023).

[2] Hirai, H. et al. *Prog Earth Planet Sci* 10, 3 (2023)

[3] Komatsu, K., Machida, S., Noritake, F. et al. *Nat Commun* 11, 464 (2020)

[4] Proeba, T., Andriambarijaona L., et al. *in preparation* (2024) .

A novel experimental methodology for investigating the growth kinetics and porous structure of surfactant-promoted gas hydrate

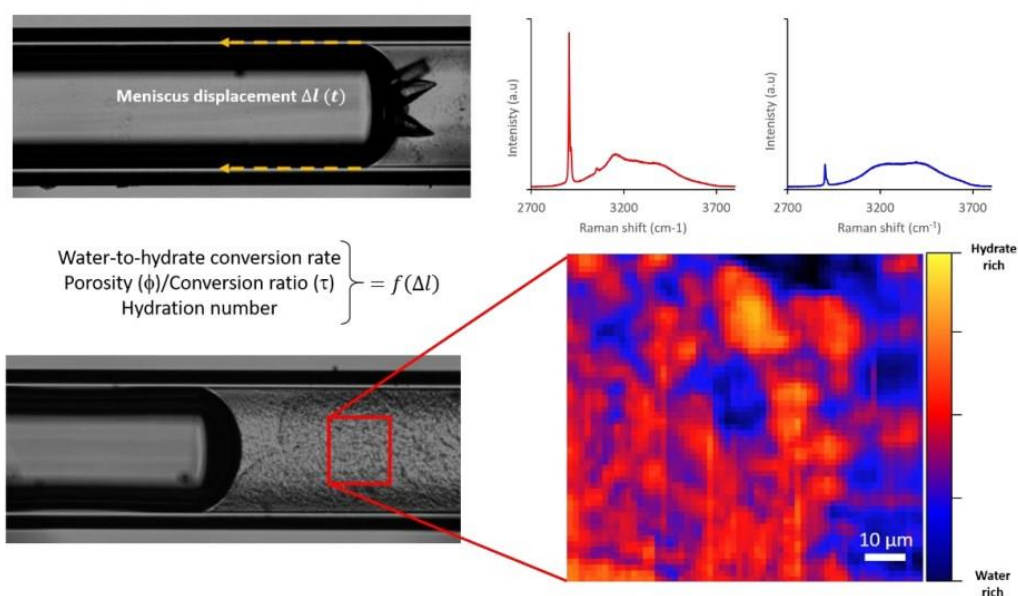
Belkacem Samar¹, Saphir Venet¹, Arnaud Desmedt^{2,3}, Daniel Broseta¹

¹ *Laboratoire des Fluides Complexes et leurs Réservoirs (LFCR), UMR 5150 CNRS-Université de Pau et des Pays de L'Adour, 64000 Pau, France*

² *Institut des Sciences Moléculaires, UMR 5255 CNRS-Université de Bordeaux, Talence, France*

³ *Laboratoire Léon Brillouin, UMR12 CEA-CNRS, Gif-sur-Yvette, France*

We show how important properties of gas hydrates can be determined quantitatively by optical microscopy coupled with Raman spectroscopy observations carried out in a thin glass capillary with proper temperature and pressure control. This determination is made possible by the one-dimensional geometry and the large aspect ratio (internal diameter vs. length), that allow the position of the water/guest interface to be monitored precisely together with the generation and growth of hydrate crystals. We have been able to demonstrate that SDS and AOT-promoted methane hydrate forms a porous skeleton, which is built from the hollow methane hydrate crystals that are continuously generated at the interface between methane and the aqueous SDS solution (Venet et al. 2022). Raman spectroscopy measurement permits to show that the SI methane hydrate making up the skeleton has cage occupations similar to those in the absence of SDS and AOT.



New Insights into the self-preservation phenomenon of methane hydrates

Belkacem Samar¹, Saphir Venet¹, Arnaud Desmedt^{2,3}, Daniel Broseta¹

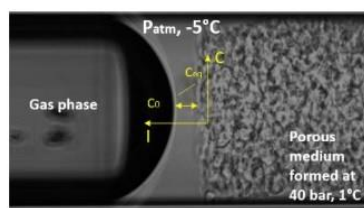
¹ Laboratoire des Fluides Complexes et leurs Réservoirs (LFCR), UMR 5150 CNRS-Université de Pau et des Pays de L'Adour, 64000 Pau, France

² Institut des Sciences Moléculaires, UMR 5255 CNRS-Université de Bordeaux, Talence, France

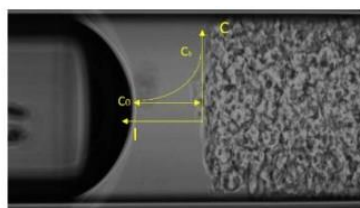
³ Laboratoire Léon Brillouin, UMR12 CEA-CNRS, Gif-sur-Yvette, France

Within a certain range of temperature below 0°C, gas hydrates have the unique property of metastably preserving themselves when pressure is lower than the equilibrium value, say, a few bar or even at atmospheric pressure, i.e. far outside their stability zone. This phenomenon, referred to as “anomalous preservation” or “self-preservation”, is characterized by an extremely slow rate of dissociation of gas hydrates which can be preserved for weeks (Stern et al. 2001). The studies of this phenomenon have been carried out mostly with methane hydrates in macro-reactors, and a tentative explanation for such a stability is that the hydrates are covered with an ice layer (or “ice shield”) that serves as a diffusive barrier and thus prevents the guest molecules to escape through the ice. Even though ice seems to play a role on the phenomenon of self-preservation, the ice-shield theory has been facing a lot of skepticism as it is considered that the sole presence of an ice layer is not sufficient to contain the guest molecules and withstand the pressure induced by the liberation of the gas initially enclathrated.

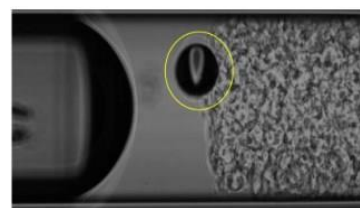
In this work, we monitor, by means of a novel experimental methodology that enables us the observation by optical microscopy of hydrates in thin glass capillary cells (High pressure Optical Cells – HPOC), the dissociation of methane hydrates into methane-saturated supercooled water. To our surprise, anomalous preservation of methane hydrates in the absence of ice is also possible. The melting of a porous, surfactant-promoted hydrate induces the formation of a thin water film whose thickness increases slowly over time. Micro-Raman spectroscopy experiments confirm the presence of a dissolved methane concentration gradient within this film which increases over time until a methane bubble nucleates and grows near the hydrate – the water film is then expelled far from the skeleton as a lamella, and the process of water film generation and thickening starts again. This process can be explained by considering the methane’s diffusive transport from the hydrate skeleton to the surface of the water/methane meniscus, which becomes too slow for large enough water films: the concentration of dissolved methane then exceeds the supersaturation limit of water and a gas bubble nucleates and grows as shown in the figure below



1st period: Hydrates dissociate into supercooled water supersaturated with methane



2nd period: The thickness of the supercooled water film doesn't permit methane to diffuse through it quicker than hydrates to dissociate.



Final period: Concentration of methane in supercooled water reach a critical value that triggers nucleation of gas bubble.

Self-preservation of methane hydrates at -5°C and ambient pressure, where the average dissociation rate is two orders of magnitude lower than normal.

Risk management for natural gas-hydrogen blend hydrate formation in pipeline transport

Jeong-Hoon /Sa¹, Sang-Gyu /Cho², Joonwoo /Seo³

¹ Department of Chemical Engineering, Dong-A University, Busan, South Korea, jhsa@dau.ac.kr

² Offshore Plant Resources R&D Center, Korea Institute of Industrial Technology, Busan, South Korea, sgcho96@kitech.re.kr

³ Department of Chemical Engineering, Dong-A University, Busan, South Korea, 2271113@donga.ac.kr

The transport of hydrogen-natural gas blends (HNGB) through pipelines is a promising way of economic hydrogen transport utilizing the already established pipeline networks. While hydrogen can penetrate the pipeline metal surfaces, limiting its concentration up to 20% can prevent the risk of brittleness. Under typical operating conditions of HNGB transport, clathrate hydrates, crystalline solid compounds formed by water and gas, would form and cover the pipe surface, causing a large pressure drop and thus considerably reducing the transport efficiency. Although the moisture is primarily removed before injection, it tends to accumulate in the bent or curved sections of the pipelines by the intermittent operation. Here, to evaluate the risk of hydrate formation during HNGB transport, phase equilibrium conditions of HNGB hydrates were measured by mixing 10% or 20% hydrogen into a synthetic model natural gas mixture (CH₄ 97%/C₃H₈ 3%). The addition of hydrogen shifts the hydrate formation conditions to the low temperature regions by ~1.5 K, but HNGB hydrates can still form as long as the moisture is present. The effects of thermodynamic inhibitors (NaCl and monoethylene glycol), which can minimize the hydrate formation risk, were also examined. The addition of 15 wt% NaCl was found to decrease the hydrate formation temperatures by 7.7 K, implying the permanent prevention of hydrate formation when considering the operating conditions of HNGB transport. The excellent reliability of the measured phase equilibrium data was demonstrated by the linear regression and consistency tests for the hydrate dissociation enthalpy and water activity. In addition, the potential risk of HNGB hydrate formation during pipeline transport was evaluated using the rock-flow cell, which is often used for flow assurance studies. Effects of driving force ($\Delta T = 5\text{--}15$ K) and water content (0.3~10%) on HNGB hydrate formation were characterized in terms of the amount of gas uptake, water to hydrate conversion, and morphological observation of hydrate deposition behavior. Changes in gas composition upon HNGB hydrate formation were also analyzed using the online gas chromatography. Based on the experimental results, efficient strategies for risk management of HNGB transport were proposed. These results will be applicable to design an efficient HNGB transport process and establish the optimal operating strategy with a successful risk management of hydrate formation.

Towards storing and transporting gases in the hydrate form

Matvei Semenov¹, Abdolreza Farhadian¹, Ulukbek Mirzakimov¹, Andrey Stoporev^{1,2}, Mikhail Varfolomeev¹, Roman Pavelyev¹

¹ Department of Petroleum Engineering, Kazan Federal University, Kazan, xotoy_82@mail.ru

² Department of Physical and Colloid Chemistry, Gubkin University, Moscow

One of Barry Commoner's four "laws of ecology" says, "Nature knows best." And nature decided to store vast methane reserves in solid form in gas hydrate deposits. In this regard, two significant challenges arise for the scientific community – developing a safe technology for extracting methane from gas hydrate deposits and creating an environmentally friendly technology for storing and transporting gas in the hydrate form. On the first call, countries without significant hydrocarbon reserves collaborate closely, actively studying gas hydrate deposits and developing technologies for methane extraction. For example, countries like Japan, China, Korea, the United States, and Singapore have significantly advanced in hydrate gas production.

The second challenge is to develop a technology for storing and transporting natural/associated gases in the hydrate form as an alternative or addition to existing technologies such as pipeline transport, compressed natural gas, and liquefied natural gas. Following the given scientific and technical task, our group creates eco-friendly hydrate formation promoters and carriers based on available biological compounds. The designed chemicals and hydrate-forming media have efficiently accelerated methane hydrate growth [1, 2]. Studies are being conducted considering the effect of promoter concentration, water content in a carrier, thermobaric conditions, and protocol for obtaining hydrates [3]. Fast kinetics of gas hydrate growth, high storage capacity, high stability of hydrates formed, and no foam formation in the gas recovery stage are key factors in commercializing hydrate-based gas storage technology. The effects of gas hydrate promoters on the environment and living cells should also be considered. To address these critical issues, castor oil was used to synthesize four novel biosurfactants (BSCOs) to accelerate the rate of methane hydrate formation and increase its storage capacity [1]. The results showed that the water-to-hydrate conversion in the presence of BSCOs was 97 % in only 9.5 min without foam formation. Additionally, a maximum conversion of 89.1 % was achieved in 3.5 wt% NaCl solution, indicating the potential of BSCOs to enhance methane hydrate formation in saline water. Furthermore, only 7.5–10.5 % of the methane hydrate stored at 1 atm and -5 °C were dissociated during 14 days, making the hydrates formed in the presence of BSCOs prospective for methane storage and transportation. This study presents a way to design an efficient hydrate formation promoter with no foaming and the hydrate capable of self-preservation, taking into account the environmental challenges of hydrate-based methane storage technology.

With oil and gas production shifting towards the Northern regions and the Arctic shelf, effective development of these reserves requires new approaches due to harsh conditions such as low reservoir temperatures, specific environmental requirements, and insufficient infrastructure. The formation of gas hydrates has the potential to clog wells, damage equipment, and reduce the efficiency of technological systems. Therefore, it is essential to understand the mechanisms of gas hydrate formation and develop methods and technologies to employ these compounds for the benefit of humanity. For this purpose, joint scientific and technical surveys are conducted with oil and gas-producing companies to tame the gas hydrates for storing and transporting different gases.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation under agreement No. 075-15-2022-299 within the framework of the development program for a world-class Research Center «Efficient development of the global liquid hydrocarbon reserves».

Reference

1. Farhadian A. et al. Sulfonated Castor Oil as an Efficient Biosurfactant for Improving Methane Storage in Clathrate Hydrates // ACS Sustain Chem Eng. Vol. 10, № 30. P. 9921–9932.
2. Gong Y. et al. Carriers for Methane Hydrate Production: Cellulose-Based Materials as a Case Study // ACS Sustain Chem Eng. Vol. 10, № 31. P. 10119–10131.
3. Semenov M.E., Mirzakimov U.Z., Stoporev A.S. Effect of Promoters on Methane Hydrate Formation Under Static Conditions // Chemistry and Technology of Fuels and Oils. Springer, 2023.

Hybrid Promoters for Synergistic Enhancement of Thermodynamic Stability of Methane Hydrates

Jiwoong Seol¹

¹ Faculty of Liberal Education, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 08826, Republic of Korea; e-mail : seoljiwoong@snu.ac.kr

For hydrate-based energy storage (HBES) technology, this study introduces a novel method to improve the thermodynamic stability of methane hydrates using two thermodynamic promoters. Initially, the structure and equilibrium conditions of CH₄ hydrate containing a novel sH promoter, cyclooctanone (cOct=O), were determined. Subsequently, by adding a well-known sH promoter, cyclooctane (cOct), the structure and equilibrium conditions of the (cOct + cOct=O + CH₄) hydrate were investigated. Compared with the conventional promoter cOct, the novel promoter cOct=O exhibited a higher promotion capacity. Surprisingly, the mixture of cOct and cOct=O exhibited an even higher promotion capacity than cOct=O alone. In other words, the promotion capacities followed the order of cOct < cOct=O < (cOct + cOct=O) (Figure 1). This synergistic promotional effect due to a simple combination of any two promoters has not been previously reported. The results of this study indicate that specific combinations of promoters can serve as “hybrid promoters,” synergistically improving the thermodynamic stability. The findings of this study propose a breakthrough for sustainable HBES technology in terms of both energy efficiency and cost-effectiveness. They also broaden the applicability of gas hydrates and provide new perspectives for gas hydrate thermodynamics.

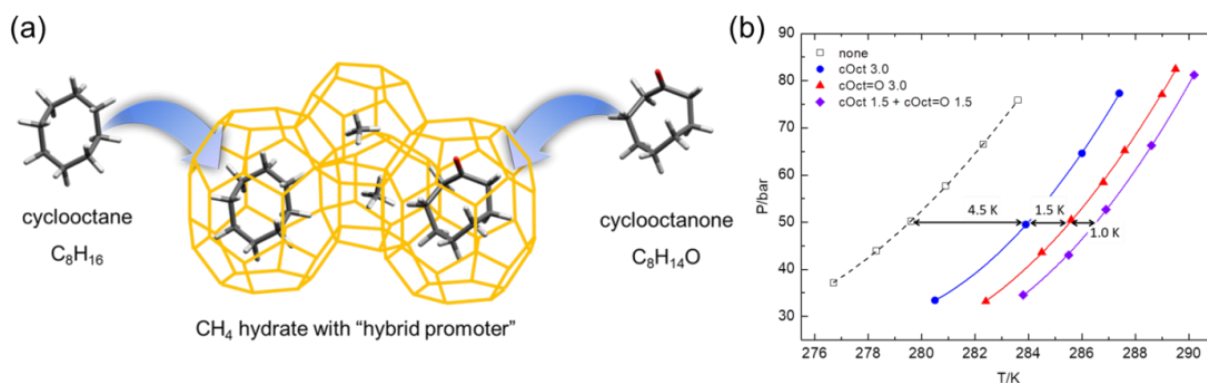


Figure 1. (a) Schematic of a homogeneous CH₄ hydrate containing both cOct and cOct=O ; (b) Equilibrium P–T curves. The equilibrium temperatures of the [cOct (3.0 mol%) + CH₄] (blue) and [cOct=O (3.0 mol%) + CH₄] (red) hydrates are 4.5 K and 6.0 K higher than those of pure CH₄ hydrate (black), respectively. However, the equilibrium temperatures of [cOct (1.5 mol%) + cOct=O (1.5 mol%) + CH₄] hydrate (purple) are even 1.0 K higher than those of the [cOct (3.0 mol%) + CH₄] hydrate.

This work was supported by the Basic Science Research Program funded by the Ministry of Education (2017R1D1A1B03033000 and 2022R111A1A01068394).

HyPurTex: Elevating Textile Wastewater Purification for Sustainable Production

Subhash Kumar Sharma*, Rajnish Kumar

Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai-600036, India

*Corresponding author: subhash@smail.iitm.ac.in

Keywords: Textile industry, effluents, gas hydrate, water purification, sustainability, HyPurTex.

Abstract

The textile industry, a cornerstone of global manufacturing, faces substantial challenges in managing wastewater and ensuring sustainable water practices. This study addresses the pressing issues associated with the treatment of industrial effluents from textile processes, emphasizing the need for innovative and efficient technologies. Water resource management profoundly impacts economic, environmental, and societal dimensions, necessitating responsible approaches to address pollutants originating from textile production. Conventional wastewater treatment methods in the textile industry often encounter drawbacks such as high operational costs, substantial sludge generation, and prolonged treatment durations. To overcome these challenges, a pioneering gas hydrate-based process for water purification and recycling is proposed. This method leverages the phase change from liquid to solid to facilitate the removal of contaminants, presenting a promising alternative for the textile sector. The study investigates the impact of various textile-related pollutants, including dyes, chemicals, and suspended solids, on the equilibrium thermodynamics and kinetics of a gas mixture relevant to the proposed process. Parameters such as color, chemical oxygen demand (COD), total dissolved solids (TDS), and other key indicators are examined to assess the efficacy of the gas hydrate-based treatment. Preliminary findings reveal that the proposed gas hydrate-based process demonstrates notable potential for addressing the unique challenges posed by textile industry effluents. The equilibrium characteristics of the gas mixture, influenced by textile pollutants, exhibit trends similar to those observed in other industrial contexts. The study provides crucial insights into the thermodynamics and kinetics of the gas hydrate formation process under textile-related pollutant conditions. This research lays the groundwork for the development of a sustainable and cost-effective technology tailored to the specific demands of textile wastewater treatment. The study's outcomes contribute essential data to advance the understanding and application of gas hydrate-based processes in the textile industry, marking a significant step towards achieving water sustainability in textile manufacturing.

Cation and anion effects of imidazolium based ionic liquids on methane hydrate formation

Suhyeon/Son¹, Jonghwan/Lee², Jeong-Hoon/Sa³

¹ Department of Chemical Engineering, Dong-A University, Busan, South Korea,

093031@donga.ac.kr

² Department of Chemical Engineering, Dong-A University, Busan, South Korea,

jhwanlee10@gmail.com

³ Department of Chemical Engineering, Dong-A University, Busan, South Korea, jhsa@dau.ac.kr

The use of additives is essential in utilizing hydrates for practical applications with enhanced economic feasibility. Ionic liquids are a class of hydrate additives that have a great potential, and they function as thermodynamic or kinetic inhibitors/promoters depending on their molecular structure and/or concentration. It has been known that imidazolium-based ionic liquids act as dual function inhibitors for CH₄ hydrate formation. In general, as the length of the alkyl chain of the imidazolium cation increases, the hydrophobicity increases, and thus the inhibition effect decreases. The type of anions can also affect the kinetics of hydrate formation due to several factors, primarily affecting the level of interactions with surrounding water molecules. In this study, imidazolium-based ionic liquids were synthesized with cations of different lengths of alkyl chains ([C₄MIM]⁺, [C₈MIM]⁺, [C₁₂MIM]⁺) and anions of Cl⁻ or FeCl₄⁻, and their effects on CH₄ hydrate formation were examined. To investigate the effect of ionic liquids on CH₄ hydrate formation, subcooling temperature (ΔT) at the onset of hydrate nucleation in 'fresh water' and 'memory water' was measured. While no particular trend was found in fresh water tests, but with memory water, the subcooling temperature in the presence of [C₁₂MIM][Cl] was the lowest ($\Delta T = 2.9K$), followed by the [C₁₂MIM][FeCl₄] ($\Delta T = 3.9K$), and both cases showed lower ΔT values than 'pure water' ($\Delta T = 4.2K$) systems. With the other ionic liquids ([C₈MIM][Cl], [C₄MIM][FeCl₄], [C₈MIM][FeCl₄]), ΔT was higher than the pure water case. Interestingly, it was confirmed that foam was generated in the presence of [C₁₂MIM][Cl] or [C₁₂MIM][FeCl₄]. Also, ionic liquids having Cl⁻ anion had lower ΔT values than those having FeCl₄⁻, suggesting that [C₁₂MIM]⁺ has the potential to function as a kinetic promoter, acting like a surfactant. In the gas uptake measurement experiment, the [C₁₂MIM]⁺ based ionic liquid also showed a faster formation rate than the pure Water system. In particular, [C₁₂MIM][FeCl₄] had an initial gas uptake (~1h) value about 6 times higher than that of pure water, acting as a potential hydrate kinetic promoter. These results show that ionic liquid additives can act as potential kinetic promoters or inhibitors depending on the type of cations and anions.

Prospects for hydrate-based energy storage technologies

Andrey Stoporev¹, Anton Semenov¹, Daria Sergeeva², Denis Voronin¹

¹ Gubkin University, Moscow, Russia, stopor89@bk.ru

² Skolkovo Institute of Science and Technology (Skoltech), Moscow, Russia

The development of the northern and Arctic regions presents several challenges, such as the need to develop technologies for storing and transporting natural gas and phase transition heat, ensuring the safe use of natural resources, and preventing accidents during oil and gas production caused by gas hydrates and emissions. A large energy capacity, the melting/decomposition temperature range depending on the pressure and latent heat of these processes of gas hydrates will ensure their use as containers for cold storage [1]. Thus, using these compounds makes it possible to optimize the phase change materials (PCM) for a specific process (due to the possibility of varying the stability of hydrates over a wide range). This study aims to create energy supply and saving technologies in these regions using clathrate hydrates as PCM by exploring the nucleation, growth, and decomposition of gas hydrates applied to these technologies.

Even though clathrate hydrates have negative impacts such as stopping oil and gas production and causing emergencies during their formation, these inclusion compounds can be helpful due to their ability to store a vast amount of energy by concentrating gas. Using hydrate carriers to encapsulate clathrate hydrates or increasing the water-gas contact area is a promising approach to increase their rate of formation and efficiency of PCM.

This research studied the effect of various surfactants and reactor coatings on hydrate nucleation and growth, proposing promoters based on natural compounds such as sugar, humic acids, and cellulose-based materials as media to accelerate hydrate formation. Careful selection of promoters and materials based on natural compounds can optimize the conditions for production, extract required components efficiently, and minimize harm to the fragile ecosystem. Using developed containers can also increase the mechanical strength of encapsulated materials and improve thermal conductivity for efficient energy storage.

Therefore, a comprehensive study of clathrate hydrate formation and encapsulation can offer solutions to scientific problems and provide energy and resource-saving technologies for the northern and Arctic regions, including natural gas and oil production. The introduction of these technologies can better prepare the world community for the challenges of developing the Arctic.

The study was supported by the Ministry of Science and Higher Education of the Russian Federation in the framework of the state task in the field of scientific activity; subject number FSZE-2022-0001.

[1] Delahaye, A., Fournaison, L., and Dalmazzone, D., 2018. Use of Hydrates for Cold Storage and Distribution in Refrigeration and Air-Conditioning Applications. *Gas Hydrates 2: Geoscience Issues and Potential Industrial Applications*, pp.315-358.

Optimizing Biogas Upgrading with Clathrate Hydrates: Influence of Different Water Phases and Additives

Rafal Damian Wolicki¹, Michele Ciulla¹, Serena Pilato¹, Gabriella Siani¹, Nadia Barbacane¹, Antonella Fontana¹, Samanta Moffa¹, Pietro Di Profio^{1,*}

¹ Department of Pharmacy, University "G. d'Annunzio" of Chieti-Pescara, via dei Vestini 31, 66010 Chieti, Italy.

*Corresponding author: P. Di Profio (pietro.diprofio@unich.it)

Biogas, a renewable energy source derived from organic waste, has emerged as a promising alternative to fossil fuels. However, its utilization necessitates upgrading to remove carbon dioxide (CO₂) and obtain biomethane, the primary energy carrier. Conventional upgrading methods often involve energy-intensive processes or hazardous chemicals, posing environmental and safety concerns [1].

Clathrate hydrates, ice-like crystalline structures formed under moderate temperature and pressure conditions, present a promising alternative for biogas upgrading [2]. These inclusion compounds feature a hydrogen-bonded network of water molecules that can encapsulate small guest, including methane (CH₄) and carbon dioxide (CO₂). The utilization of clathrate hydrates for biogas upgrading offers several advantages over conventional methods, since these structures are environmentally friendly, and the formation does not require harsh chemicals or extreme conditions, minimizing environmental impact. In fact, the process operates at relatively low temperatures and pressures, thus reducing energy consumption.

This work aims at the formation of hydrates for biogas separation in the presence of biphasic water-oil systems, or in the presence of particle suspensions, in order to positively influence the percentage of CO₂ captured and the overall rate of produced biomethane.

In the liquid phase, two alcohols (1-Nonanol and 1-Octanol, currently considered as environmentally friendly [3]) were used alone or with surfactants. In the suspended-aqueous phase, activated carbon, graphene oxide V30, and graphene oxide V50 were employed to assess the percentage of CO₂ enclathration, thus the purity of the residual methane.

Experiments were conducted in pressure drop conditions at 1 °C and 4 MPa. A 60% CH₄ and 40% CO₂ gas mixture was employed in a reactor, whereas surfactants, long chain alcohols and solid particles were used in the water phase to enhance hydrate formation. In order to determine the gas mixture composition before and after hydrate formation and dissociation, an IR detector was assembled by using the Premier series of IR gas sensors by Dynament (UK) for CO₂ and CH₄. Results showed 1-Nonanol outperformed 1-Octanol probably due to its lower solubility (0.13 g/L) and longer carbon chain, enabling better gas-hydrate contact and selective CH₄ capture. The experiment using only alcohols without promoters most effectively highlights this difference.

Graphene-based derivatives showed modest performance in terms of hydrate selectivity; however, they improved the formation kinetics, and considering the vast properties of graphene derivatives in terms of synthesis and functionalization, GO derivatives represents a promising avenue for advancing sustainable biogas upgrading technologies. Further research on GO's structure and function can unleash its full potential in a more efficient and environmentally friendly biogas purification process.

Bibliography

[1] J. Das, H. Ravishankar, P.N.L. Lens. *Journal of Environmental Management*, 2022, 304, 114198.

[2] P. Di Profio, V. Canale, N. D'Alessandro, R. Germani, A. Di Crescenzo, A. Fontana. *ACS Sustainable Chem. Eng.* 2017, 5, 2, 1990–1997.

Pore-scale investigation of the effect of heterogeneous permeability on CO₂ hydrate kinetics

Lifei Yan¹, Manon Schellart¹, Mahnaz Aghajianloo¹, Denis Voskov^{1,2}, Rouhi Farajzadeh^{1,3}

1. Delft University of Technology, Department of Geoscience and Engineering, Stevinweg 1, 2628 CN, Delft, the Netherlands, l.yan@tudelft.nl
2. Energy, Science and Engineering, Stanford University, USA
3. Shell Global Solutions International B.V., Grasweg 31, 1031 HW, Amsterdam, the Netherlands,

Carbon dioxide (CO₂) sequestration stands as a pivotal strategy for mitigating global greenhouse gas emissions. However, the formation of CO₂ hydrates presents a potential challenge by decreasing CO₂ injectivity and permeability in the vicinity of the wellbore. Furthermore, the intrinsic complexity of porous reservoirs, characterized by factors such as rock heterogeneity, wettability, and pore structure, poses several challenges including capillary-driven backflow and non-uniform water distribution, Figure 1. Therefore, elucidating the impact of heterogeneous permeability on the kinetics of hydrate nucleation and formation is paramount.

To address this, we conducted a series of microfluidic experiments to investigate hydrate formation and dissociation across five porous domains with varying permeabilities (ranging from 30 to 300 mD), encompassing three homogeneous pore structures and two heterogeneous structures. Employing a custom-built experimental setup, we achieved precise control over thermodynamic conditions for hydrate formation and dissociation (ranging from 0 to 40 bar and 0.1 to 30 °C). High-resolution cameras enabled the dynamic capture of pore-scale hydrate formation and growth, with kinetics quantified accordingly. Dissociation dynamics were similarly captured through controlled thermal processes.

Our experimental findings revealed two distinct types of hydrate formation: formation at moving CO₂-water interfaces and formation predominantly within the water phase. The former behavior occurred during CO₂ displacement of water, while the latter occurred at static interfaces between CO₂ and water. Crucially, we observed that permeability played a pivotal role in shaping hydrate patterns within porous media of varying pore sizes, with the resulting solid hydrate occupying approximately 7.4% of pore space in the 30 mD porous domain. Furthermore, analysis of two heterogeneous regions within a single chip revealed contrasting water distribution and hydrate formation patterns. This study contributes to a deeper understanding of the dynamics involved in hydrate formation and dissociation processes, shedding light on their complexities within porous media.

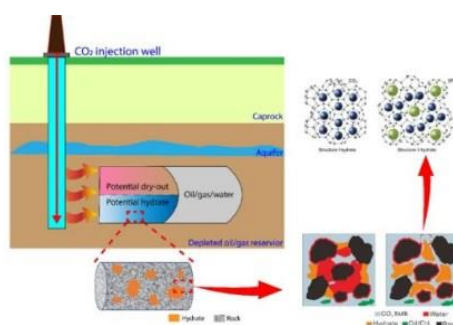


Figure 1. CO₂ hydrate formation in porous reservoir at multiple scale.

Optimizing H₂ uptake in H₂-THF hydrate and its mechanism: Implication on hydrate-based H₂ storage

Zhenyuan Yin^{1*}, Jibao Zhang¹, Yan Li¹, Yang Li¹, Yizhi Rao¹

¹Institute for Ocean Engineering, Tsinghua Shenzhen International Graduate School, Tsinghua University, Shenzhen 518055, PR China

Abstract

Hydrogen (H₂) is rapidly gaining attention as a key player in the clean energy portfolio due to the benefits of high energy density (142 MJ/kg). H₂ storage in the form of solid hydrates is considered a safe and high-energy density technology. However, severe pressure required for pure H₂ hydrate storage and the sluggish H₂ hydrate formation kinetic are still the major challenge to develop scale-up hydrate-based H₂ storage. Thus, the thermodynamic promoter tetrahydrofuran (THF) was used to alleviate the H₂ hydrate formation condition. Furthermore, the environmentally friendly kinetic promoter L-Val amino acid was coupled with THF to promote the H₂ hydrate formation kinetics. In our study, we found the final gas uptake with 0.3 wt% L-Val reached 29.83 ± 1.22 v/v at the cooling rate of 0.05 K/min, which was 115.07% higher than that without L-Val (see Fig.1a). Moreover, the optimal promoting effect of 0.3 wt% L-Val persisted when it was reused. Additionally, we systematically designed kinetic experiments with morphology observation at macro-scale complemented with micro-scale characterization of the synthesized H₂-THF hydrate. H₂-THF hydrate morphology transitioned from slurry-like in the liquid phase to plate-like at the gas-liquid interface at THF concentration (C_{THF}) = 3.5 mol% (see Fig.1b). Single H₂ molecules were identified to be enclathrated in the 5¹² small cages of H₂-THF sII hydrate for all C_{THF} based on Raman spectroscopic analysis (see Fig.1c). The co-existence and the ratio of THF hydrate and H₂-THF hydrate under various C_{THF} first reported with HP μ-DSC suggested that optimizing C_{THF} was key in achieving high H₂ gas uptake (see Fig.1d). These findings provide insights into understanding the tuning effect of thermodynamic promoters on H₂ hydrate at multi-scales and provide guidance for future large-scale hydrate-based H₂ storage applications.

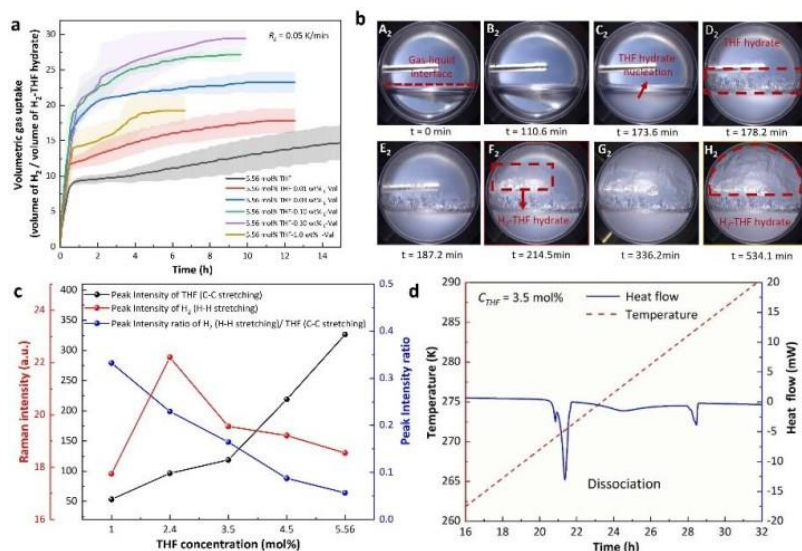


Fig.1. (a) Effect of L-Val concentration on H₂ gas uptake under various L-Val concentrations; (b) H₂-THF hydrate morphology at C_{THF} = 3.5 mol%; (c) Raman intensity of C-C stretching of THF occupying large cages and H-H stretching of H₂ occupying small cages in H₂-THF sII hydrate at all C_{THF}; (d) H₂-THF hydrate dissociation thermograms at C_{THF} = 3.5 mol%.

A dual hydrate-based desalination and CO₂ capture process: a Raman spectroscopy approach

Sadain Zafar^{1,2*}, Claire Pirim^{1,2*}, Bertrand Chazallon^{1,2*}

¹Univ. Lille, CNRS, UMR 8523 - PhLAM - Physique des Lasers Atomes et Molécules, F-59000 Lille, France, bertrand.chazallon@univ-lille.fr

²CERLA – Centre d'Études et de Recherches Lasers et Applications, F-59000 Lille, France

The confluence of global economic and population growths sets the backdrop of simmering tensions over dwindling water resources, global warming, and air pollution. Addressing the increase in CO₂ concentration in the atmosphere and, at the same time, water scarcity (SDG 6 and 13 from UN) is of paramount importance. Recently, it has been proposed that both ongoing challenges can be tackled employing the hydrate technology [1]. The working principle of this single integrated approach at the molecular scale is based on the selective trapping of CO₂ molecules (guests) in clathrate hydrate cages and, at the same time, the exclusion of the salt from growing hydrate crystals.

A unique in-situ Raman-coupled high-pressure cell is used to investigate the effect of salt (NaCl) concentration (typically of 3.5 wt%) on hydrates formation at different subcooling temperatures between +4°C and –12°C. We show how initial partial or complete CO₂ dissolution in the salt solution impact clathrate hydrates crystal morphology and distribution in the reactor [2]. More specifically, a methodology utilizing water-stretching vibrations and corresponding calibration curves was developed to derive water-to-hydrate conversion and maximal water recovery. Furthermore, a monitoring of the rise of the salt concentration in the remaining liquid phase was obtained in-situ to reveal how water is primarily extracted from the saline solution to participate in the formation of the CO₂ hydrate lattice structure. These results brought new insights into the molecular understanding of the salting-out effect by clathrate formation, and therefore is of valuable help in the development of the hydrate-based-desalination process with CO₂ capture.

[1] M. Sarshar & A. H. Sharafi, *Desalination Water Treat.*, vol. 28, no. 1–3, pp. 59–64, Apr. 2011, doi: 10.5004/dwt.2011.2201.

[2] S. Zafar PhD thesis 2024, University of Lille

Session 5: Hydrates and Astrophysics

Chair: Leonardo del Rosso, Bertrand Chazallon, Elodie Gloesener

Spectroscopic study of the methane hydrate at high pressure and temperature

Selene Berni¹, Demetrio Scelta^{1,2}, Samuele Fanetti^{1,2}, Matteo Ceppatelli^{1,2}, Roberto Bini^{1,2,3}

¹ LENS, European Laboratory for Non-linear Spectroscopy, Sesto Fiorentino, Firenze, Italy
berni@lens.unifi.it

² ICCOM-CNR, Istituto di Chimica dei Composti OrganoMetallici, Sesto Fiorentino, Firenze, Italy³
Dipartimento di Chimica “Ugo Schiff”, Università di Firenze, Sesto Fiorentino, Firenze Italy

Methane clathrate hydrates (MH) are common compounds in the Universe, and their behaviour in pressure and temperature plays an important role in both the geochemical and astrophysical fields. For instance, on Earth, the methane hydrate stability can provide information upon environmental effects due to the dissolution of the methane clathrates present at the oceans' depths^[1], while in the outer solar system, it helps understanding the release mechanisms of methane from icy planets and satellites' first inner layers into their atmospheres^[2]. Moreover, from a strictly chemical point of view, the liquid phase arising from the decomposition of the MH at high pressure and temperature is of great interest to explore the potential reactivity of water and methane triggered through two-photon irradiation. Indeed, the higher mobility of molecules in fluid phases and an eventual partial solubility generated by pressure can create favourable environments to reactivity processes^[3].

The various methane hydrates' phases are well known and characterised from a crystallographic point of view, but there are still controversies regarding the melting line of phase MH-III, for which three hypotheses are reported in literature^[4, 5, 6]. Furthermore, recent studies^[7] have evidenced a remarkable increase in the solubility of methane in water at high temperature and pressures of the GPa magnitude, providing possible hints in the quest for promising reaction conditions on these mixtures.

Here, we addressed some open issues concerning the methane hydrate using spectroscopic techniques (Raman, FTIR) as probing tools. Freshly produced MH-I samples, synthesised *ex situ* using a well assessed technique^[8] were loaded in membrane Diamond and Sapphire anvil cells (mDAC and mSAC), and sealed while cooled down at liquid nitrogen temperature, by the application of sufficient pressure to make the clathrate stable at ambient temperature. The melting lines of the three different phases of the MH were studied in mSAC using FTIR spectroscopy and following a vibration-libration combination band across the phase transition. For what concerns phase MH-III, this method allowed to observe the melting of water ice-VII and, subsequently, of MH-III, finding a remarkable agreement with the melting line proposed by Kurnosov et al^[4]. Raman spectroscopy allowed us to fully characterise phonon lattice and internal modes, finely mapping their pressure dependence. Finally, we studied the miscibility of methane in water in the melted phase. Our results clearly show that solubility is much lower than expected from recent literature^[7], and substantially in agreement with the simulation by Duan et al^[9]. Anyway, a high P - high T area of the phase diagram was found where a probable increase in solubility is observed, and that could provide ideal conditions for induced reactivity studies^[10].

[1] Kvenvolden, K. A.; *Chemical geology* 71 (1988) 41.

[2] Choukroun, M. et al.; *Icarus* 205 (2010) 581.

[3] Bini, R.; Schettino, V.; Imperial College Press: London (2013).

[4] Kurnosov, A. et al.; *Z. Naturforsch B: J. Chem. Sci.* 61 (2006) 1573.

[5] Bezacier, L. et al.; *Phys. Earth Planet. In.* 229 (2014) 144.

[6] Kadobayashi, H. et al.; *J. Raman Spectrosc.* 51 (2020) 2536.

[7] Pruteanu, C. et al.; *Sci. Adv.* 3 (2017) e1700240.

[8] Fanetti S., et al.; *J. Phys. Chem. C* 124 (2020) 10159.

[9] Duan, Z. et al; *Geochim. Cosmochim. Acta* 70 (2006) 3369.

[10] Scelta D., et al.; *J. Phys. Chem. C* 126 (2022) 19487.

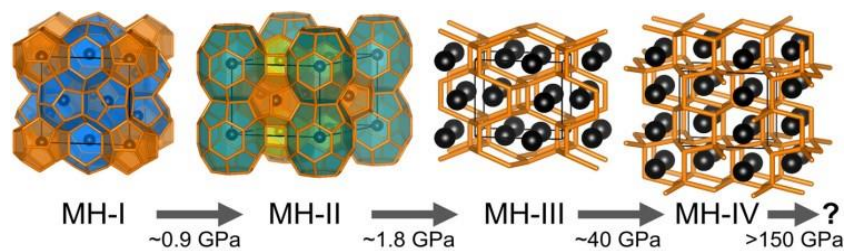
Exploring the stability and new structures of gas filled ices up to Mbar pressures

U. Ranieri¹, S. Di Cataldo¹, L. Monicelli², M. Rescigno^{1,2}, R. Gaal², L.E. Bove^{1,2,3}

¹Physics Department, Università di Roma La Sapienza, Piazzale Aldo Moro 5, 00196, Roma, Italy

²LQM, Physics Department, EPFL, SB-PH station 3 Lausanne, Switzerland

³IMPMC, CNRS-UMR 7590, Sorbonne Université, 75252 Paris, France



Gas hydrates are both interstellar and on outer planets and moons [1-3]. Under the p-T conditions experienced in these medium-size icy bodies, clathrate hydrates adopt filled ice structures whose stability range and properties are still largely unexplored [4-8]. Methane and hydrogen hydrates are also expected to be present under very high pressures (up to 200 GPa) in giant icy planets interiors such as in Uranus or Neptune and largely determine their chemistry and conductivity properties. 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, N₂) [8,9,10] filled ices under the extreme conditions experienced in the large ice bodies of our solar system.

[1] O. Mousis et al., *Space Sci Rev* 174, 213–250 (2010) ; *Astrobiology* 15, 4 (2015)

[2] I. De Pater and J.J. Lissauer, *Planetary Sciences*, Cambridge University Press 2004

[3] L. E. Bove et U. Ranieri, *Phil. Trans. R. Soc. A* 377: 0262 (2019).

[4] J.S. Loveday et al., *Nature* 410, 661 (2001).

[6] W. L. Mao et al. *Science* 297, 2247 (2002) ; *Phys. Today* 60(10), 42 (2007).

[7] L. De Rosso et al., *Nature Comm.* 7, 13394 (2016) ; *Nature Materials*, 1-6 (2020).

[8] S. Schack et al., *PNAS* 116 (33) 16204-16209 (2019).

[9] U. L. Ranieri, et al., *PNAS* 120 (52) e2312665120 (2023).

[10] S. Beni, et al., under submission (2024).

Methane Outgassing from Clathrate Hydrates on Titan: Partial Dissociation and Substitution Mechanisms

Elodie Gloesener¹, Mathieu Choukroun¹, Tuan H. Vu¹, Ashley G. Davies¹, Arnaud Desmedt²,
Christophe Sotin³

¹ Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, United States
(elodie.d.gloesener@jpl.nasa.gov), ² Institut des Sciences Moléculaires, Talence, France, ³ Nantes
Université, Laboratoire de Planétologie et Géosciences, Nantes, France

Laboratory experiments [1] have shown that methane clathrate hydrates can be formed on Saturn's largest moon, Titan, whose substantial nitrogen-methane atmosphere (1.5 bar) and cold temperatures (92-94K) allow CH₄ clathrates to be thermodynamically stable from its surface down to the base of its hydrosphere. Clathrate hydrates are believed to play a significant role in the hydrocarbon cycle on Titan and could contribute to the replenishment of atmospheric methane [1-3]. Ammonia, an important clathrate inhibiting agent, is known to cause partial melting of water ice between the eutectic point at 176 K (at 1 bar) and the liquidus temperature, and could potentially promote cryovolcanism through the decomposition of the surrounding clathrate hydrates in Titan's icy shell. Methane could also be released from clathrate reservoirs via substitution by ethane [4-5].

In order to better assess the contribution of clathrates to methane outgassing and exchange processes on Titan, we carried out Raman spectroscopic investigations of the CH₄-C₂H₆ replacement kinetics in clathrate hydrates at pressure and temperature conditions relevant to Titan. Our results show the successful formation of ethane clathrate hydrates from the reaction of liquid ethane with methane clathrates and ice. We also studied the phase behavior of the ternary H₂O-THF-NH₃ system between 90 K and 270 K using cryogenic X-ray diffraction and Raman spectroscopy and the H₂O-CH₄-NH₃ system using differential scanning calorimetry. Our study confirms the phase diagram of the H₂O-THF-NH₃ system [6] with the presence of multiple phase transitions. The novel THF-NH₃-rich phase is observed below 215 K with a refined unit cell suggesting a trigonal lattice [7]. Our preliminary calorimetry data show a partial dissociation behavior in agreement with previous Raman spectroscopy studies [8].

Significant methane outgassing on Titan may therefore occur without requiring extensive cryovolcanic eruptions. The presence of small amounts of ammonia in the subsurface could potentially trigger partial dissociation of methane clathrates on warming and lead to a gentle, non-explosive and, gradual release of methane to the atmosphere. Our results support the hypotheses that liquid ethane can be trapped in Titan's subsurface, and that methane could be released as ethane replaces it in clathrate hydrates.

Acknowledgements: This work has been conducted at JPL/Caltech, under contract with NASA. Government sponsorship acknowledged. Copyright 2024. All rights reserved.

References: [1] Choukroun, M. et al. (2010) *Icarus*, 205, 581-593. [2] Lunine J. I. and Stevenson D. J. (1987) *Icarus*, 70, 61–77. [3] Tobie G. et al. (2006) *Nature*, 440, 61-64. [4] Choukroun M. and Sotin C. (2012) *Geophys. Res. Lett.*, 39, L04201. [5] Vu T. H. et al. (2020) *Geophys. Res. Lett.*, 47, e2019GL086265. [6] Muñoz Iglesias V. et al. (2018) *ACS Earth Space Chem.*, 2, 135-146. [7] Gloesener, E. et al. (2023) *ACS Earth Space Chem.*, 7, 1162-1171. [8] Petuya et al. (2020) *Chem. Commun.*, 56, 12391–12394.

Gas hydrates as indicators of cryomagmatic processes on Ocean worlds

Victoria Muñoz-Iglesias¹, Gabriel Tobie¹, Benoit Jabaud¹, Erwan Le Menn¹, Olivier Bollengier¹
¹ Nantes Université, Univ Angers, Le Mans Université, CNRS, Laboratoire de Planétologie et Géosciences, LPG, UMR 6112, France (victoria.munoz-iglesias@univ-nantes.fr)

Europa and Ceres show evidence of surface activity potentially related to subsurface aqueous reservoir and suggesting recent eruption of cryomagmas (brines and ice slurries) [1-5]. However, the existence of cryomagmatic activity and associated degassing has not yet been clearly identified. One way to detect such activities is from clathrate signatures. The icy crusts are mainly composed of water ice, but it is possible that other volatiles such as CO₂ and CH₄, salts and clay minerals are present mixed with the ice. Under pressure, in the subsurface, CO₂ and CH₄ can be trapped in the form of gas hydrates. Thermal, tectonic, and cryomagmatic activity may entrain gas hydrates to the surface.

Dissociation of gas hydrates during the ascent may also favor eruption processes. Europa and Ceres lack an atmosphere, their surfaces are in high vacuum (below 10⁻⁴ bar) and low temperatures (around 90 - 150 K). Therefore, gas hydrates reaching the surface will slowly dissociate over time. Thus, there will be a period of time in which recently erupted gas hydrates will be detectable by both remote and in situ measurements, allowing confirmation of recent cryomagmatic events. Salts and clays affect both clathrate stability and spectroscopic signatures [6, 7]. Recent observations by the James Webb Space Telescope identified significant quantities of CO₂ correlated with a region enriched in chlorinated salts, implying an internal origin [8-9]. This suggests that CO₂-rich gas hydrates and salty brines may be involved in the cryomagmatic systems on Europa.

The stability and dissociation kinetics of gas hydrates in the presence of different types of salts and clays is currently being determined at LPG by reflectance-IR and Raman spectroscopy. These spectra will aid in the interpretation of data from the Dawn at Ceres, JUICE and Europa Clipper missions at Europa. Previously, we have studied the formation of clathrates in certain complex mixtures. Understanding what happens during formation in the interior will help to interpret the spectroscopic signatures under surface conditions. In this regard, we have carried out several studies with CH₄, CO₂ and THF clathrates in the presence of different salts such as NaCl, NH₄Cl, MgSO₄, and clays such as montmorillonite (Mt) and kaolinite (Kaol). Specifically, we have studied by calorimetry at pressures up to 100 bar, representative of pressure in the icy crusts of Europa and Ceres, separately, the systems (a) CH₄ clathrate-MgSO₄-Mt-Kaol, and (b) CO₂ clathrate-NaCl-NH₄Cl, and by calorimetry and spectroscopy at 1 bar the systems (c) THF clathrate-MgSO₄/NaCl/NH₄Cl/Mt/Kaol. Consistent with previous works [10-12], we observed that salts and clay minerals can reduce the nucleation time of gas hydrates but inhibit subsequent growth due to several factors such as increased metastability phenomena in the form of supercooled liquids, salting-out effects when salts were present, gas adsorption on clay surfaces, and reduction of available space. The next step now is to understand their dissociation processes during ascent and to acquire reflectance-IR and Raman spectra of gas hydrates in presence of salts and clays in order to identify their respective signatures at surface conditions, in order to compare with existing and future space data. First results on the CO₂-NaCl system will be presented at the conference.

Refs: [1] Roth et al. 2014, *Science* 343, 171–174; [2] Ruesch et al. 2016, *Science* 353, aaf4286; [3] Sparks et al. 2016, *Apj* 829, 121; [4] Jia et al. 2018, *Nat. Astron.* 2, 459–464; [5] McCord and Zambon 2019, *Icarus* 318, 2–13; [6] Park et al. 2014, *Environ. Sci. Technol.* 48, 6597–6603; [7] Tao et al. 2020, *Energies* 13, 231; [8] Villanueva et al. 2023, *Science* 381, 1305–1308; [9] Trumbo and Brown 2023, *Science* 381, 1308–1311; [10] Park and Sposito 2003, *J. Phys. Chem. B* 107, 2281; [11] Wang et al. 2023, *Chem. Eng. J.* 451, 138757; [12] Ren et al. 2023, *Appl. Energy* 340, 120997.

Ammonia incorporation in methane clathrate within the subsurface ocean of Titan

S. Nozaki^{1,2}, Y. Sekine², G. Tobie³, Y. Liang⁴, T. Tsuji⁴ and H. Genda²

¹Department of Earth and Planetary Sciences, Tokyo Institute of Technology, Tokyo, Japan, nozaki@elsi.jp, ²Earth-Life Science Institute, Tokyo Institute of Technology, Tokyo, Japan,

³Laboratory of Planetology and Geosciences, Nantes University, CNRS, Nantes, France,

⁴Graduate School of Engineering, The University of Tokyo, Tokyo, Japan

Titan's building materials in the circum-Saturnian disk would have contained CH₄ and NH₃ as solids due to the low temperatures [1]. These CH₄ and NH₃, together with thermally decomposed CH₄ from organics in the rocky core [2], would have been present in the subsurface ocean [3]. In the thermal evolution, the thickness of Titan's icy crust would have changed over time, forming/dissociating CH₄ clathrate hydrates at the interface with the subsurface ocean [3]. If NH₃ in the ocean might have been incorporated into the clathrate structure, this would affect the physical and chemical properties of the subsurface ocean. However, the incorporation of NH₃ into CH₄ clathrates remains controversial [4,5].

Here, we examine incorporation of NH₃ into CH₄ clathrates using molecular dynamics simulations of GROMACS and molecular models [e.g., 6]. The cage compositions of clathrates were investigated for various NH₃ concentrations in solution. The initial configurations of the simulations were three-phase coexistence of a NH₃ solution (828 molecules for H₂O and 0–30% NH₃), supercritical CH₄ (144 molecules), and pure CH₄ clathrate as a seed (828 and 144 molecules for H₂O and CH₄, respectively). Isothermal-isobaric (NPT) simulations at 200 MPa and 270 K corresponding to Titan's subsurface ocean were conducted using the Nosé-Hoover thermostat and the Parrinello-Rahman barostat.

We find that a significant fraction of NH₃ is incorporated into clathrates together with CH₄ as both host and guest molecules for all NH₃ concentrations assumed in this study. The cage occupancy of NH₃ becomes optimal at 40% for a NH₃ solution with 10% of NH₃ concentration. The cage occupancy of NH₃ increases with the NH₃ concentration in solution until 10% of NH₃. Beyond 10%, the cage occupancy of NH₃ decreases with increasing NH₃ concentration. The decrease in the cage occupancy may happen because the growth rate of clathrate becomes low due to limited availability of H₂O beyond 10% of NH₃. This may increase contact chances of CH₄ with clathrate surface, lowering the efficiency of NH₃ incorporation. Alternatively, high NH₃ concentrations would increase the CH₄ solubility in solutions. This may enhance an incorporation of CH₄ in clathrates, possibly lowering the cage occupancy of NH₃.

On Titan and icy dwarfs, even for an initial NH₃/H₂O fraction of ~1–2% (compatible with cometary abundances), NH₃ in the subsurface ocean can reach 5–10% and more as the icy crust thickens through time [3,7]. This could lead a prolonged subsurface ocean due to the low eutectic point of NH₃ solution [7]. Our results suggest that NH₃ can be efficiently incorporated in the icy crust through formation of clathrates, which should limit the NH₃ concentration increase in the ocean as the icy crust thickens. The incorporation of ammonia in clathrates will also favor their destabilization once advected near the surface [8], thus providing a new mechanism to generate ammonia-rich cryolavas and associated methane release on Titan and Pluto [9]. Thermal evolution models introducing our results would reveal self-consistent compositions of the icy crust and ocean, offering a linkage between the building materials and the current interior structure of Titan and beyond.

References: [1] Alibert & Mousis (2007), *A&A*, 465, 1051. [2] Reynard & Sotin (2023) *EPSL*, 612, 118172. [3] Tobie et al. (2006) *Nature*, 440, 61. [4] Petuya et al. (2020) *Chem. Comm.*, 56, 12391. [5] Ripmeester & Alavi (2022) *Chem. Comm.*, 58, 4095. [6] Abraham et al. (2015) *SoftwareX*, 1-2, 19. [7] Nimmo et al. (2016) *Nature*, 540, 94. [8] Choukroun et al. (2010), *Icarus*, 205(2), 581-593. [9] Dalle Ore et al. (2019) *Sci. Adv.*, 5, eaav5731.

Gas separation and storage in mixed clathrate hydrates as studied by molecular simulations: Applications to astrophysical contexts

Antoine Patt¹, Julien Joliat², Jean-Marc Simon³, Sylvain Picaud²

¹ DIPC, Universidad del País Vasco, San Sebastián, Spain, antoine.patt@ehu.eus

² Institut UTINAM, Université de Franche-Comté, Besançon, France

³ Laboratoire ICB, Université de Bourgogne, Dijon, France

Beyond Earth, natural clathrate hydrates are conjectured to be present in various extraterrestrial environments, especially on other planets and/or their satellites in the Solar system. So called mixed clathrate hydrates (i.e. trapping more than one guest species) are also thought to form in those environments and some species are preferentially trap compared to others. Studying this selective trapping can provide useful explanations to observations and indirect constraints on thermodynamic conditions and atmospheric compositions when considering the celestial bodies holding clathrate hydrates. Indeed, the structural properties and trapping capabilities of gas hydrates have now been invoked in many planetology models.

Computer simulations based on an atomic-scale description of the systems under consideration have appeared as a promising tool to characterize the composition and the stability of clathrates. In this respect, calculations performed on the grand canonical (μ, V, T) ensemble, where the number of trapped molecules can vary in the simulations, is a particularly suitable tool for characterizing the fraction of the enclathrated gases in the different types of cages, which is one of the most important sought after data. Moreover, molecular simulations constitute a decisive tool to complement already well-established experiments and thermodynamic modelling by more easily accessing extreme thermodynamic conditions typical of astrophysical environments.

In this presentation, investigations concerning the gas storage and, especially, the separation power of clathrates, related to astrophysical environments mainly using the relevant Monte Carlo techniques, will be detailed. Namely, the case of the CO-N₂ mixed hydrates, relevant to help explain the [CO]/[N₂] ratio observed on the comet 67P/Churyumov-Gerasimenko will be presented. And then, through a trip to Titan, the link between CH₄-C₂H₆ mixed hydrates and the composition of the seas at the surface of this satellite of Saturn, will be explicated.

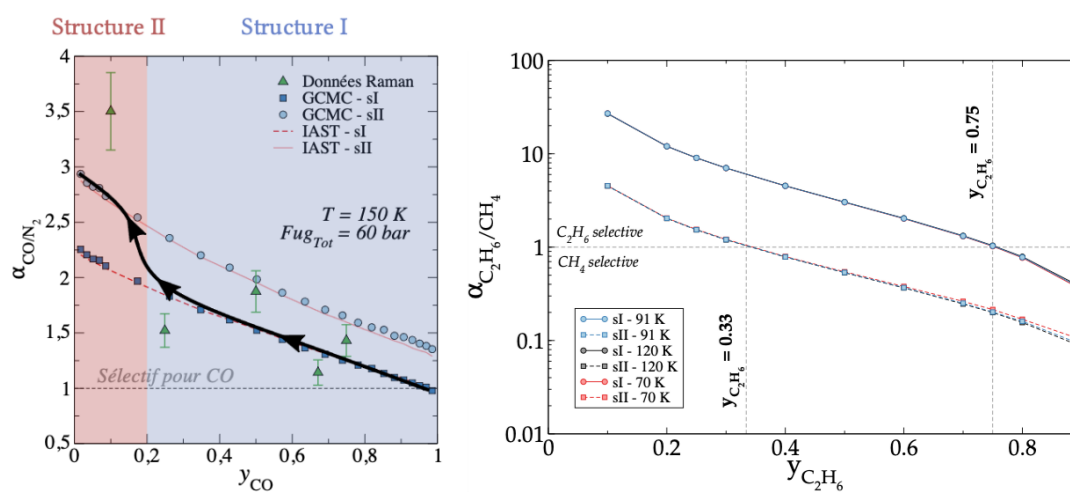


Figure 1: Molecular selectivity of the CO-N₂ (left panel) and of the CH₄-C₂H₆ (right panel) mixed hydrates

Aghajanloo Mahnaz, 37, 88
 Agnissan Art-Clarie Constant, 38
 Ahmadi Pezhman, 54
 Ait Blal Abdelhafid, 56
 Allen Christopher, 12
 Andrade Cristina, 21
 Andriambariarijaona Leon, 78
 André Xavier, 38
 Arca Simone, 19, 32
 Arndt Sandra, 45

 Babu Ponnivalavan, 58
 Bajocco Matteo, 19
 Ballenegger Vincent, 2, 10
 Bangs Nathan, 53
 Barbacane Nadia, 33, 59, 61, 87
 Barile Gianluca, 19
 Barone Ilaria, 44
 Bartels Jeremy, 20, 25
 Bassani Carlos, 3
 Batur Josip, 39
 Bento Joaquim, 53
 Berni Selene, 92
 Bertoldi Dalton, 34
 Bertoni Claudia, 41
 Bialas Jörg, 50
 Bini Roberto, 92
 Bollengier Olivier, 95
 Bordes Emilie, 7
 Bouillot Baptiste, 4, 13, 14
 Boumaiza Houaria, 57
 Bove Livia, 78
 Bove Livia Eleonora, 93
 Brancatelli Giuseppe, 46
 Broseta Daniel, 15, 79, 80
 Buccolini Marco, 32
 Burgass Rod, 54
 Burwicz-Galerie Ewa, 40
 Busetti Martina, 46

 Cabral Fagner, 21
 Cai Xinrui, 60
 Cameirao Ana, 28–30
 Camerlenghi Angelo, 41, 51
 Castellani Beatrice, 42, 76
 Cavalli Stella, 28
 Celli Milva, 6
 Ceppatelli Matteo, 92
 Chapoy Antonin, 54
 Chazallon Bertrand, 59, 61, 63, 90
 Chen Haoqi, 22, 24, 26
 Chen Mingqiang, 43

 Chies Agnese, 44
 Cho Sang-Gyu, 67
 Cho Sang-Gyu Cho, 81
 Choukroun Mathieu, 94
 Ciulla Michele, 33, 59, 61, 87
 Civile Dario, 46
 Clain Pascal, 64, 77
 Coffin Richard, 50
 Colognesi Daniele, 6
 Contreras-Reyes Eduardo, 53
 Corradin Cristina, 41
 Czamlar Valentin, 5

 D'alessandro Emilio, 19, 32
 Da Silva Marco José, 27
 Dalmazzone Didier, 77
 Daraboina Nagu, 58
 Dariva Claudio, 54
 Davies Ashley G., 94
 Davy Bryan, 50
 De La Fuente Ruiz Maria, 45
 De Vasconcelos Luiz Fernando Santos, 23, 34
 Dehghani Peyman, 62
 Del Rosso Leonardo, 6
 Delahaye Anthony, 64, 77
 Desmedt Arnaud, 7, 68, 72, 79, 80, 94
 Di Cataldo Simone, 93
 Di Profio Pietro, 33, 59, 61, 87
 Dos Santos Eduardo Nunes, 27, 28
 Douzet Jérôme, 13, 30

 E. M. Morales Rigoberto, 34
 Engel Michael, 3
 English Niall, 11, 12

 Fandino Olivia, 38, 47
 Fanetti Samuele, 92
 Farajzadeh Rouhi, 37, 88
 Farhadian Abdolreza, 82
 Ferrando Nicolas, 73
 Fidel-Dufour Annie, 29
 Fidler Lilli-Ruth, 8
 Fontana Antonella, 33, 87
 Forlin Edy, 46
 Fournaison Laurence, 64, 77
 Frah Dounya, 7

Fu Qiang, 43
 Gaal Richard, 78, 93
 Gang Li, 49
 Ge Yang, 43
 Geletti Riccardo, 46
 Genda Hidenori, 96
 Giustiniani Michela, 41, 44, 53
 Gland Nicolas, 62
 Gloesener Elodie, 94
 Go Woojin, 68
 Gon Saugata, 20
 Gong Jing, 17, 22, 24, 26
 Gravanis G., 66
 Guo Enqi, 22, 24, 26

 Haeckel Matthias, 40
 Haidar Rima, 63
 He Zhongjin, 74
 Heidari Atousa, 47
 Herri Jean-Michel, 4, 13, 14, 29, 30
 Hillman Jess, 50
 Hofer Thomas S., 8

 Istomin Vladimir, 52

 Jabaud Benoît, 95
 Jean Antoine, 38
 Jeong Siyoon, 48
 Jiang Guosheng, 74
 Joliat Julien, 97
 Jones Regan, 20, 25

 Kakitani Ofuchi Celina, 23, 34
 Keasler Victor, 20
 Khirallah Rihab, 64
 Kim Doyeon, 65
 Klocker Johannes, 8
 Kou Xuan, 49
 Kumar Rajnish, 84
 Kyriakides A.-S., 66

 Lavallo Gianluca, 28–30
 Le Hoang Hong Minh, 64
 Le Menn Erwan, 95
 Le Vourc'h Damien, 38
 Lecolier Eric, 62
 Lee Jonghwan, 67, 85
 Lee Jonghyuk, 68
 Lee Yohan, 68
 Leoni Alfiero, 19
 Lesage Nicolas, 29
 Li Qingping, 43
 Li Shouding, 70

 Li Xiao, 70
 Li Yan, 69, 89
 Li Yang, 89
 Li Yuxuan, 70
 Liang Yunfeng, 96
 Liao Najia, 17
 Linga Praveen, 71
 Lipari Vincenzo, 46
 Liu Lihao, 17, 22, 24, 26
 Liu Xuejian, 69
 Loerting Thomas, 8
 Longo Jean P. N., 27
 Lucas Elizabete, 21
 Lucente-Schultz Rebecca, 20, 25
 Lyu Chaohui, 43

 M. Fernández-Fernández Angel, 47
 Machado Vitor, 28
 Macnaughtan Michael, 50
 Maghsoodloo Saheb, 73
 Maldonado Paul, 28
 Marcelino Neto Moisés, 23, 27, 28, 34
 Martin-Gondre Ludovic, 9, 72
 Martínez Piñeiro Manuel, 47
 Marín-Moreno Héctor, 45
 Meko Fotso Victoire, 72
 Meneghel Lino Luiz, 29
 Meric Ilker, 39
 Metoyer Corbin, 20, 25
 Mi Fengyi, 74
 Minshull Tim A., 45
 Mirzakimov Ulukbek, 82
 Moffa Samanta, 33, 87
 Mohammad Taghinejad Esfahani Sadegh, 37
 Monacelli Lorenzo, 93
 Morales Rigoberto, 23, 27
 Morales Rigoberto Eleazar Melgarejo, 28
 Moro Olivia, 2, 10
 Morodei Francesco, 19
 Moulto Othonas A., 74
 Munoz-Iglesias Victoria, 95

 Nad Karlo, 39
 Naeiji Parisa, 11
 Naukanova Madina, 4, 30
 Ndiaye Papa, 54
 Nicolini Andrea, 42
 Ning Fulong, 74
 Nozaki Shunsuke, 96

 Obhodas Jasmina, 39
 Omran Ahmed, 56, 76
 Orlic Zeljko, 39

Ornella Massi, 4
 Osswald Véronique, 64, 77
 Ouyang Qian, 75
 Ozturk Onur, 4

 Pan Mengdi, 11, 12
 Pandey Jyoti Shanker, 75
 Pang Jiangtao, 74
 Pang Weixin, 43
 Park Seongah, 31
 Passucci Claudio, 19
 Patt Antoine, 97
 Pavelyev Roman, 82
 Pecher Ingo, 50
 Pelleau Pascal, 38
 Petteruti Ernesto, 32
 Picaud Sylvain, 72, 97
 Pilato Serena, 33, 59, 61, 87
 Pirim Claire, 59, 61, 63, 90
 Popeney Christopher, 20
 Poreba Tomasz, 78
 Posch Paul, 8
 Pérez Rodríguez Martín, 47

 Quaranta Andrea, 32

 Radola Bastien, 12
 Ranieri Umbertoluca, 93
 Rao Yizhi, 69, 89
 Reginaldo Natan, 27
 Rescigno Maria, 78, 93
 Riccucci Leonardo, 51
 Rossi Federico, 42
 Roy Clément, 4
 Ruffine Livio, 38, 47, 62

 Sa Jeong-Hoon, 31, 48, 65, 67, 81, 85
 Saavedra Sébastien, 64
 Sadia Shaiek, 4
 Salehy Yasmine, 64
 Salon Stefano, 51
 Salvalaglio Matteo, 60
 Samar Belkacem, 79, 80
 Sauli Chiara, 46
 Scelta Demetrio, 92
 Schellart Manon, 88
 Sekine Yasuhito, 96
 Semenov Anton, 52, 86
 Semenov Matvei, 82
 Seo Joonwoo, 81
 Seo Yongwon, 68
 Seol Jiwoong, 83
 Sergeeva Daria, 52, 86

 Serikkali Angsar, 13, 14
 Serris Eric, 29
 Sharma Subhash, 84
 Shi Bohui, 17, 22, 24, 26
 Shin Yebom, 67
 Siani Gabriella, 33, 61, 87
 Silveira Kelly, 21
 Simon Jean-Marc, 97
 Siquin Anne, 7, 62
 Sirino Thales Henrique, 34
 Son Suhyeon, 85
 Song Shangfei, 17, 22, 24, 26
 Sotin Christophe, 94
 Stoikos A., 66
 Stoporev Andrey, 52, 82, 86
 Stornelli Vincenzo, 19
 Stott Lowell, 50
 Strachan Lorna, 50
 Striolo Alberto, 60
 Sudac Davorin, 39
 Sui Jinhao, 17
 Sum Amadeu, 3, 23, 28

 Tang Anh Minh, 62
 Tariq Mohammad, 47
 Tavares Frederico, 54
 Terzariol Marco, 38
 Tinivella Umberta, 41, 44, 51, 53
 Tobie Gabriel, 95, 96
 Tohidi Bahman, 35
 Torres Larissa, 54
 Touil Abdelhafid, 15
 Trento Everton, 27
 Trigkas D., 66
 Tsimpanogiannis Ioannis N., 66
 Tsuji Takeshi, 96

 V. M. Rocha João, 34
 Valkovic Vladivoj, 39
 Valtchev Valentin, 56, 76
 Varfolomeev Mikhail, 82
 Vargas-Cordero Ivan, 53
 Vaunat Jean, 45
 Venet Saphir, 79, 80
 Villar-Munoz Lucia, 53
 Vlugt Thijs J.h., 74
 Von Solms Nicolas, 75
 Voronin Denis, 86
 Voskov Denis, 37, 88
 Voutetakis S., 66
 Vu Tuan H., 94

 Wagner Richard, 5

Wallmann Klaus, 40
Wang Yi, 49
Warnke Fynn, 50
Wen Huiyun, 43
Wilding Nigel, 2, 10
Wolicki Rafal Damian, 33, 59, 61, 87

Xiao-Sen Li, 49

Yan Lifei, 88
Yang Bo, 43
Yao Haiyuan, 17
Yarakhmedov Murtazali, 52
Yin Zhenyuan, 69, 89
Yu Zhang, 49

Zafar Sadain, 90
Zannotti Marco, 16
Zhang Jibao, 89
Zhang Peiying, 26
Zhang Xiaohan, 43
Zhang Zhaobin, 70
Zhao-Yang Chen, 49
Zhu Yumo, 17, 26
Zimmer Oliver, 5

SPONSORS



GDR2026 Hydrates de gaz

CNRS - IFREMER - ENSTA - Mines ParisTech - BRGM - IFPEN - INRAE

<http://hydrates.cnrs.fr>



OGS

Istituto Nazionale
di Oceanografia
e di Geofisica
Sperimentale

LOOKING FORWARD TO MEETING YOU IN TRIESTE!

for further info please contact

utinivella@ogs.it

