PHASE BEHAVIOR OF FLUIDS INVOLVED IN UNDERGROUND H_2 STORAGE AND SURFACE FACILITIES

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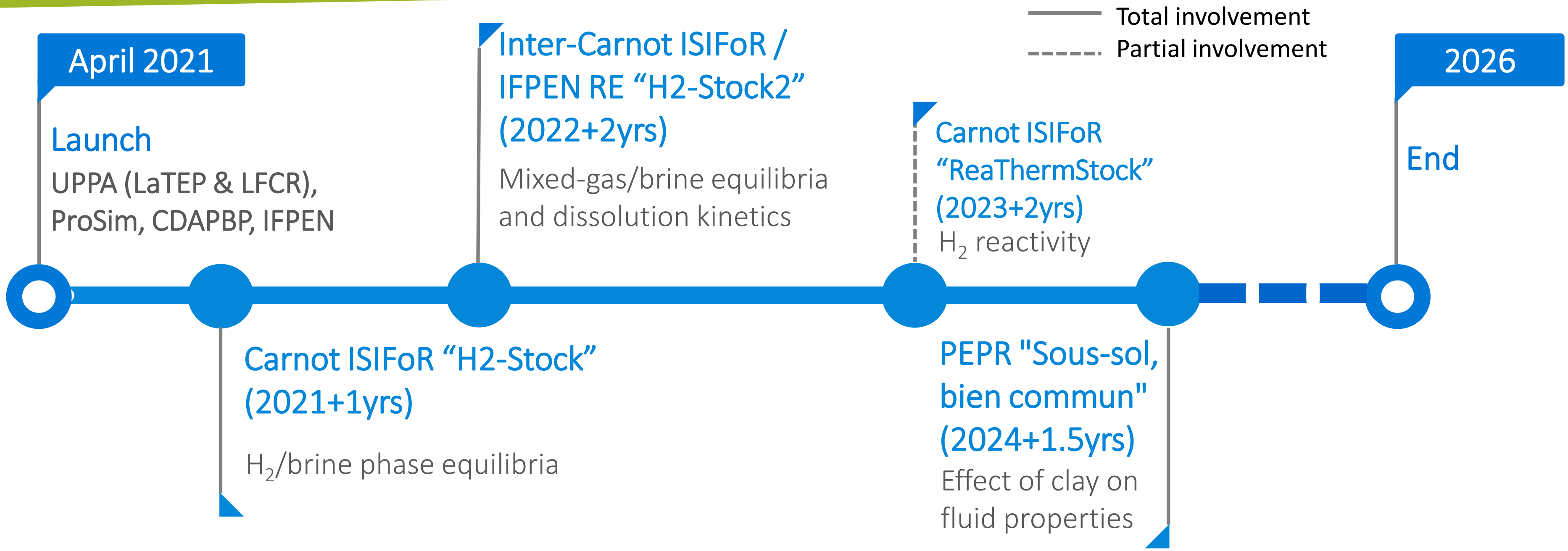
Outline

Introduction
Context
Goals

1) **PHASE BEHAVIOR OF H_2 MIXTURES**
2) **IMPLICATION ON H_2 DEHYDRATION**

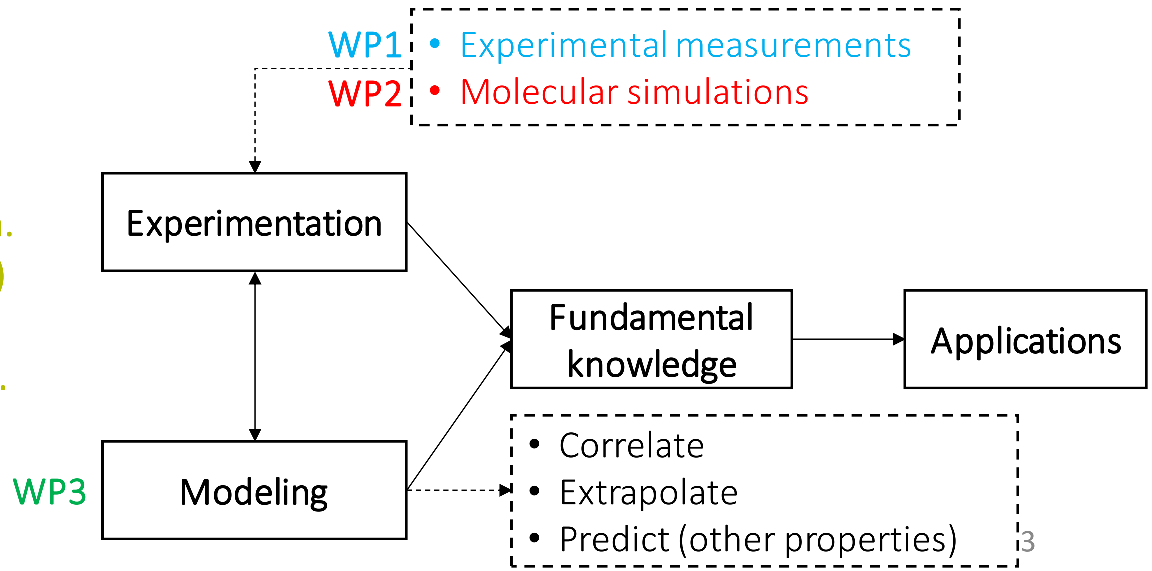
Conclusions

Research Project: Junior Chair HYDR



Research team

- Chair holder (Chabab)
- 3 permanents (Cézac, Galliero, Poulain)
- 1 PhD UPPA (nov 2021 - 2024) – Mol. Sim.
- 1 postdoc UPPA/ProSim (jan 2023 - 2025)
- 1 postdoc UPPA (dec 2023 - 2024) – Exp.
- 1 postdoc UPPA (2024 - 2025) – Mol. Sim.

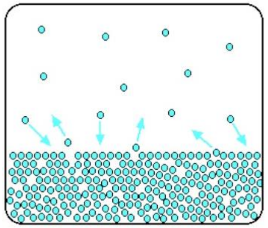


IMPORTANCE OF THERMOPHYSICAL FLUID PROPERTIES ?

Minimal effect if studied **separately**
More pronounced when studied **collectively** with **hysteresis** ? (ref: *Jadhawar et al. IJHE, 2023*)

Influencing thermo and transport properties (non-exhaustive list)

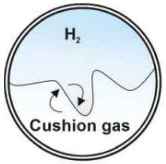
- ❖ Gas solubility and co-solubility
  - Loss through H_2 dissolution and reactivity;
  - Measuring/predicting other properties (density, IFT …)
  - Gas-mixing



- ❖ Diffusion coefficient (gas/gas & gas/liquid)
- ❖ Water content in gas
  - Dehydration process design

- ❖ Interfacial Tension (IFT)
  - Storage and Sealing capacities

- ❖ Viscosity
- ❖ Density
  - Hydrodynamics; Gas mixing, etc.

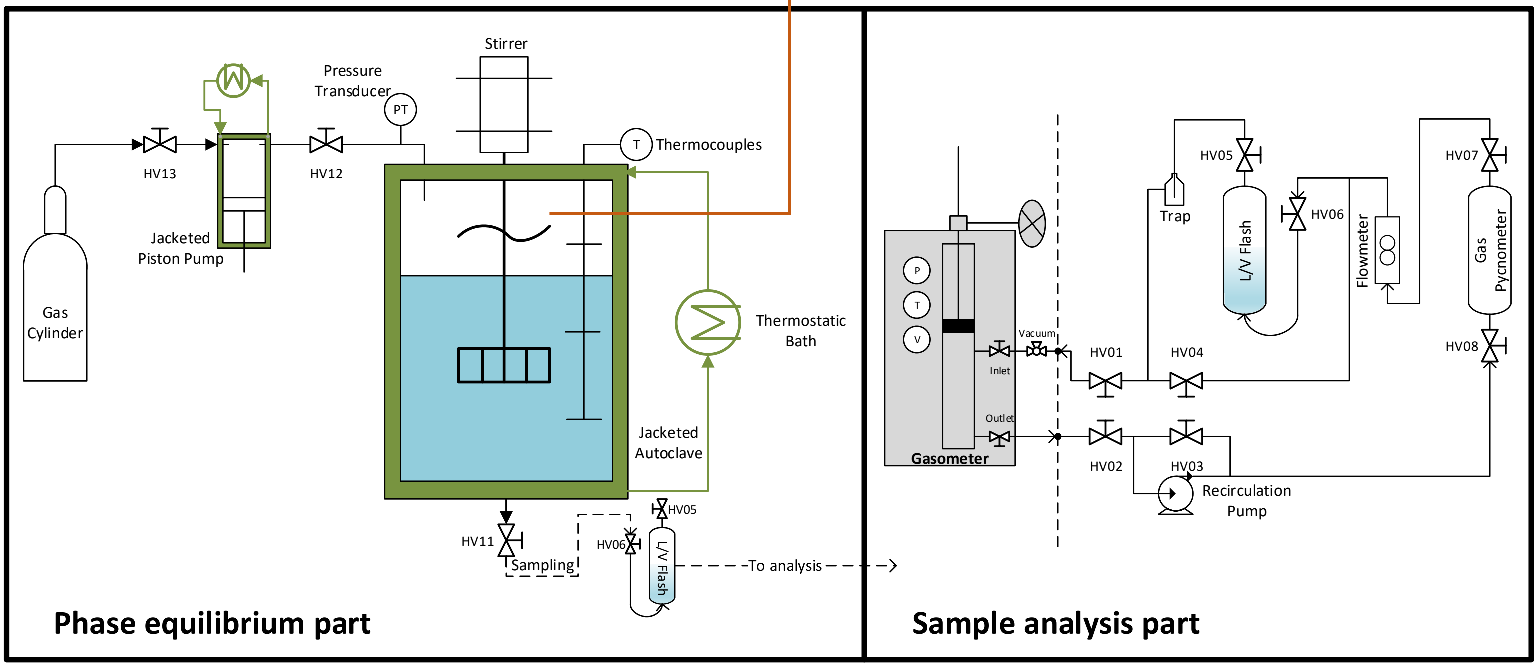


1) PHASE BEHAVIOR OF H_2 MIXTURES

I.I. Experimental aspects

a) Apparatus

+ GC & KF titration

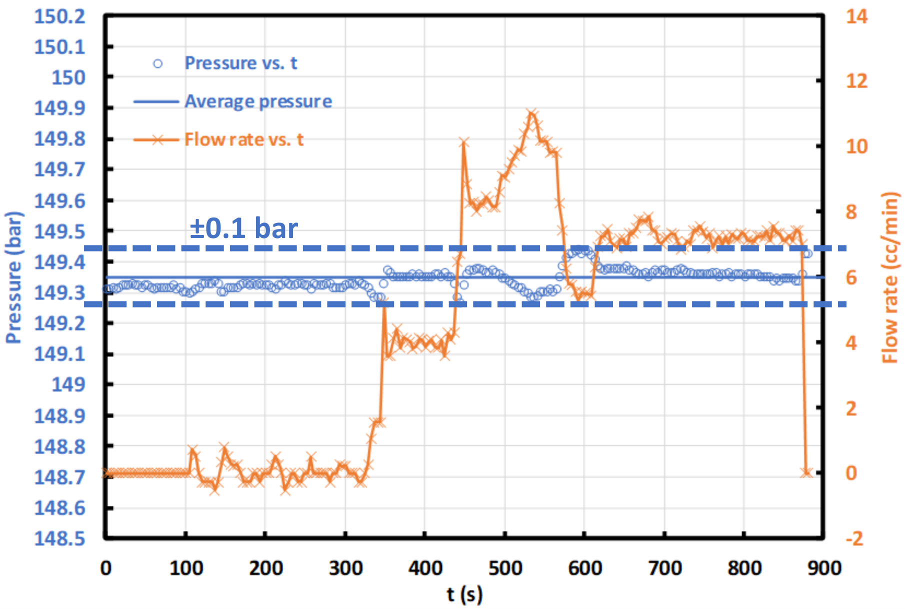


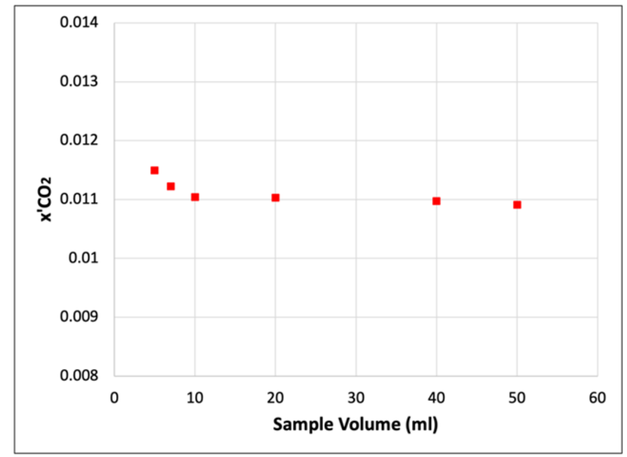
Principle of measurements of gas (pure or mixed) (co)solubility

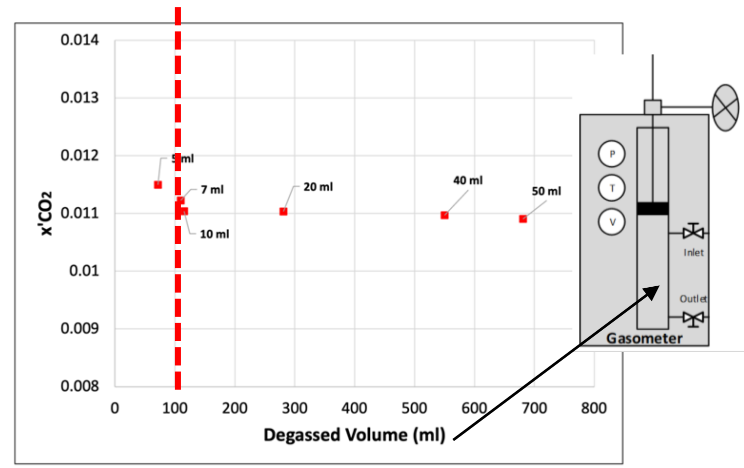
- Phase sampling, and degassing (Flash) at atmospheric conditions
- Recirculating Flash to ensure equilibrium
- Accurate volumetric and gravimetric (+GC if gas mixture) quantification of gas and liquid

I.I. Experimental aspects

b) Verifications (sampling and degassed volume)





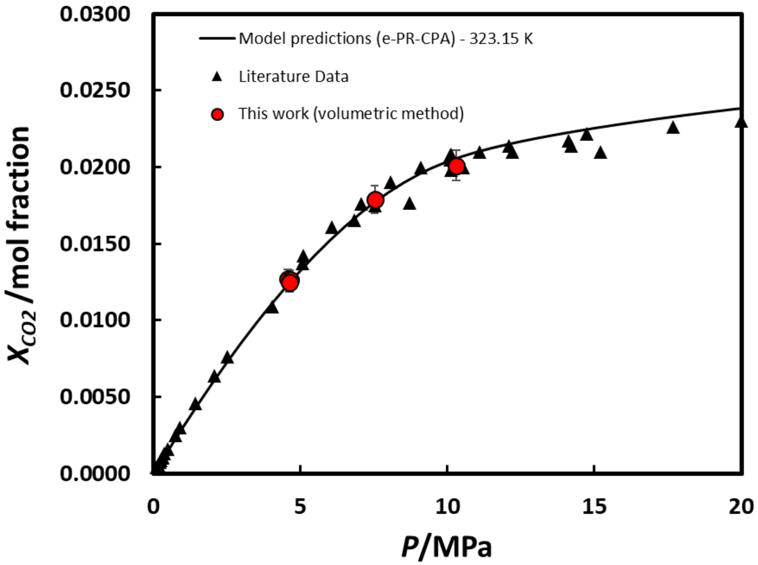


- Pressure fluctuation not exceeding 0.1 bar
- Large enough sample to have sufficient degassed volume in the gasometer

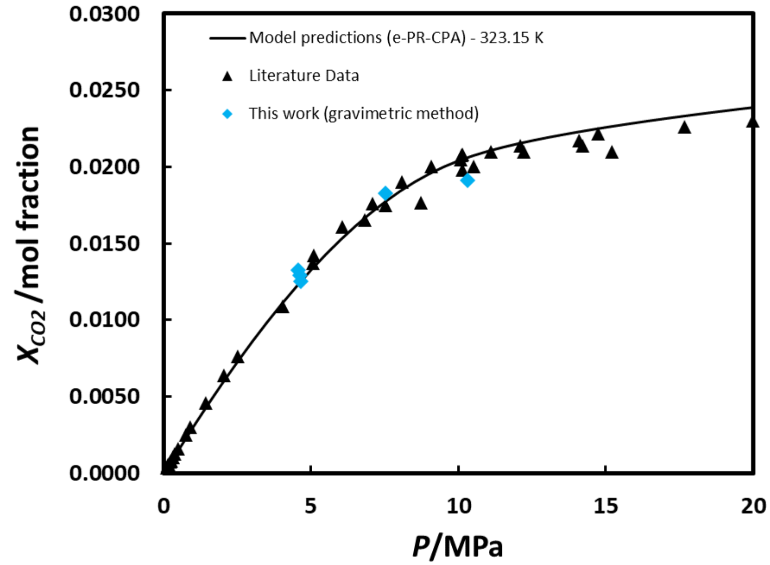
Part 1: Phase Behavior of H_2 mixtures for UHS

I.I. Experimental aspects

c) Protocol validation on CO_2+H_2O system



Method 1 : Volumetric determination



Method 2 : Gravimetric determination

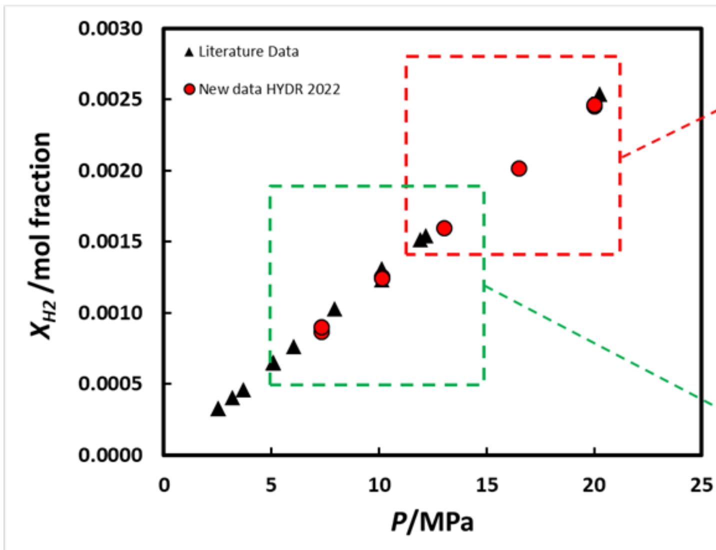
	P (MPa)	T (K)	GLR (Nm3/m3)	Sample size (g)	m_{Gas} (g)
Pt1	4.57	321.55	**15.81**	**62.85**	1.96
Pt2	4.65	323.45	**15.71**	**16.40**	0.48
Pt3	4.63	323.45	**15.65**	**26.82**	0.81
Pt4	7.53	323.15	22.95	36.15	1.58
Pt5	10.30	324.75	26.13	10.47	0.48

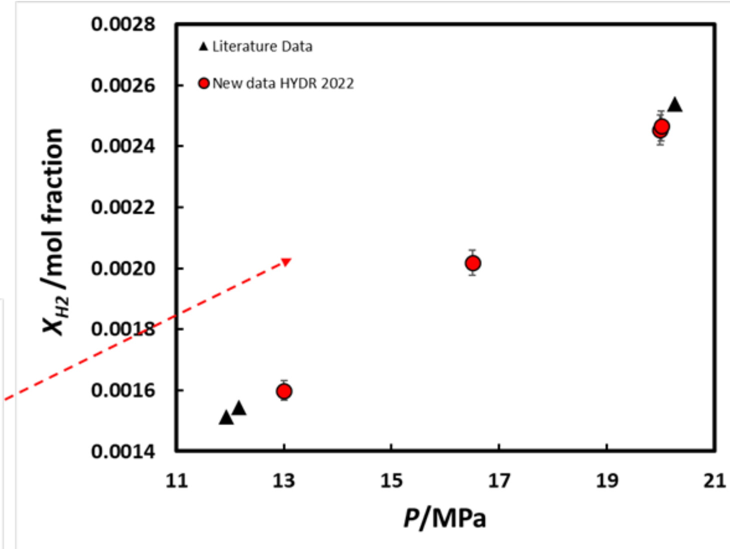
Repeatability / reproducibility check

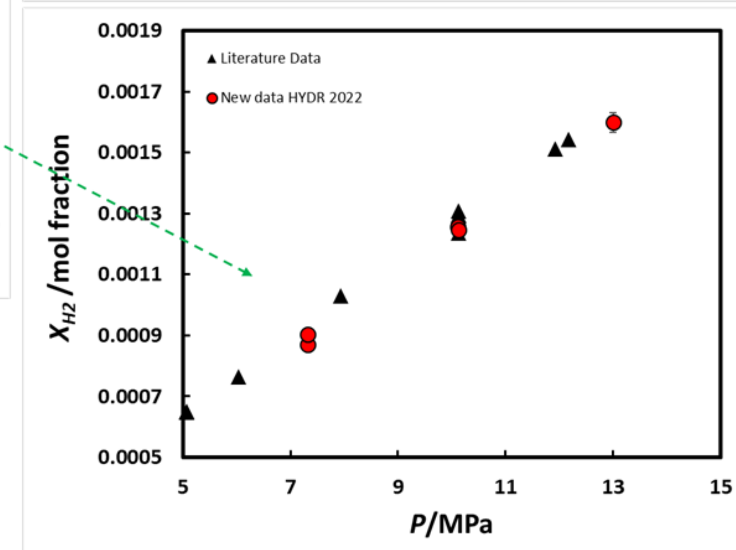
I.I. Experimental aspects

d) Measurement results

Measurements of **H_2** solubility in pure **H_2O**





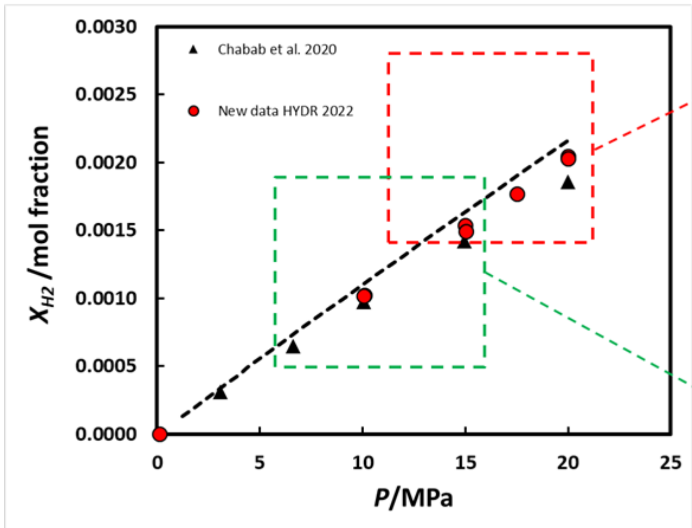


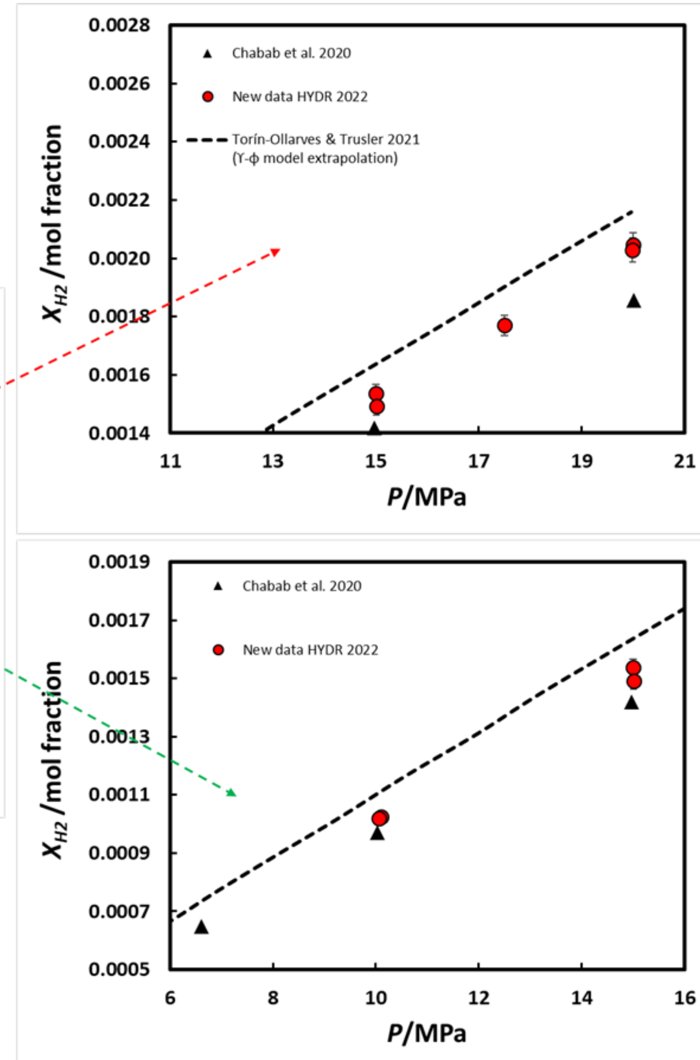
- ❑ Results **consistent** with literature data
- ❑ Due to the **low** H_2 **solubility**, measurements are **easier** at **high-pressure** (better repeatability and less uncertainty)

I.I. Experimental aspects

d) Measurement results

Measurements of **H_2** solubility in pure **1m NaCl** brine





- ❑ Our **new data** lies between the 2 existing data sources (Chabab et al. 2020 and Torín-Ollarves & Trusler 2021)
- ❑ Torín-Ollarves & Trusler 2021 and **this work** expect a **lower salting-out** than that reported by Chabab et al. 2020
- ❑ Measurements were performed up to 4 mol/kgw of NaCl

I.II. Thermodynamic modeling

Asymmetric approach (gamma-phi)

1) eNRTL-PR model (ProSim)

Liquid | Vapor

$$m_i^{aq}\gamma_i^{aq}K_i^g(T, P^{sat})\exp\left(\upsilon_i^\infty \frac{P-P^{sat}}{RT}\right) = y_i^g\varphi_i^g P$$

γ_i^{aq} → eNRTL; φ_i^g → PR EoS

2) Duan-type model

$$\ln\frac{y_{H_2}P}{m_{H_2}} = \frac{\mu_{H_2}^{l(0)}(T,P)}{RT} - \ln\varphi_{H_2}(T,P) + \sum_c 2\lambda_{H_2-c}m_c + \sum_c 2\lambda_{H_2-a}m_a + \sum_c\sum_a \zeta_{H_2-c-a}m_c m_a$$

φ_{H_2} → PR EoS

Symmetric approach (phi-phi)

Same Equation of State (EoS) for each phase

$$x_i\Phi_i^{Liq} = y_i\Phi_i^{vap}$$

3) Soreide and Whitson (SW) EoS

PR EoS with specific alpha function for water/brine and 2 different kij for liquid and vapor phases

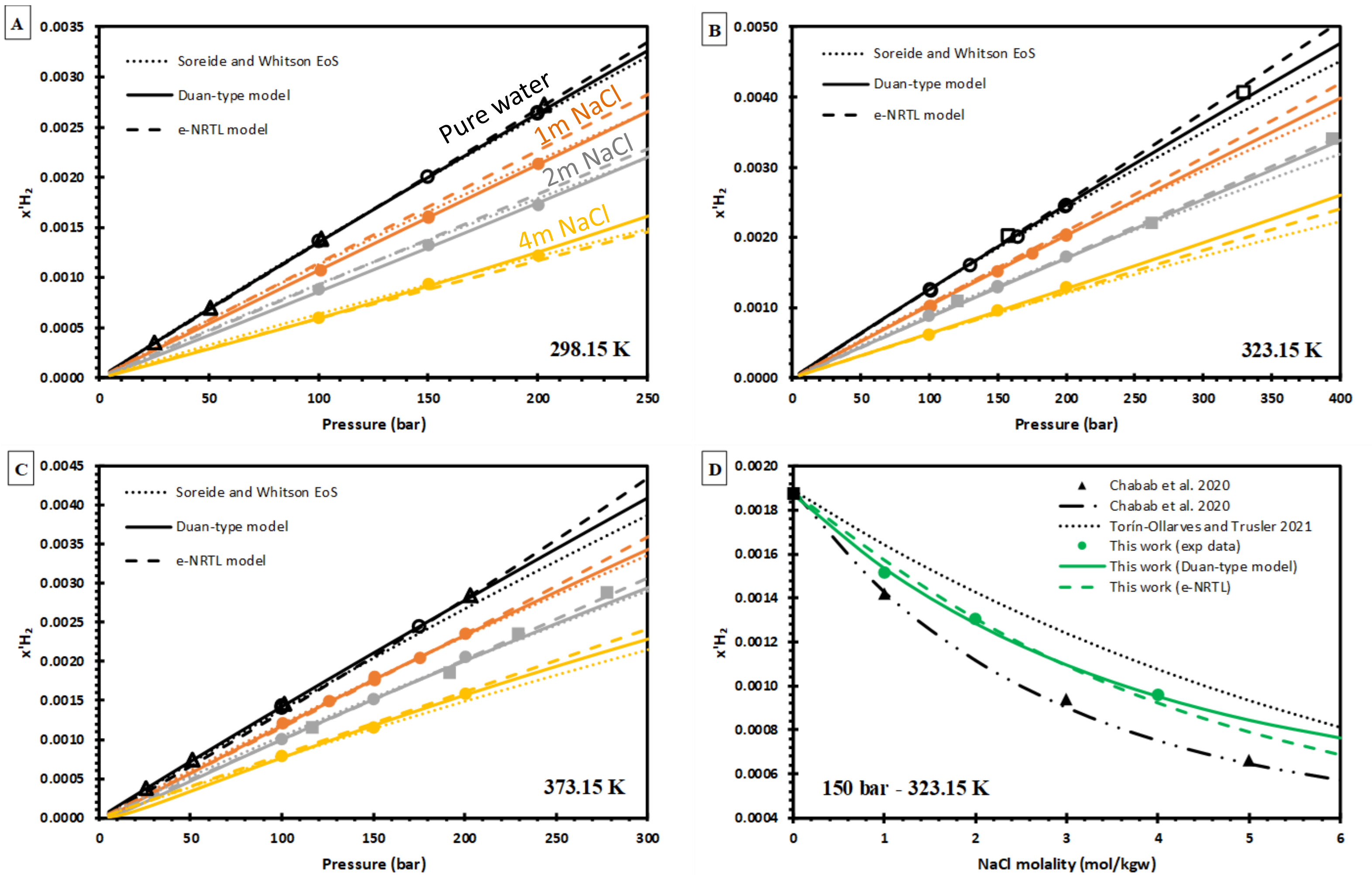
(ref : Soreide and Whitson 1992)

More details are available in:

S. Chabab, H. Kerkache, I. Bouchkira, M. Poulain, O. Baudouin, É. Moine, M. Ducousso, H. Hoang, G. Galliero, P. Cézac, Solubility of H_2 in water and NaCl brine under subsurface storage conditions: measurements and thermodynamic modeling, Int. J. Hydrogen Energy, (2023).

I.II. Thermodynamic modeling

a) Modeling results (liquid phase)



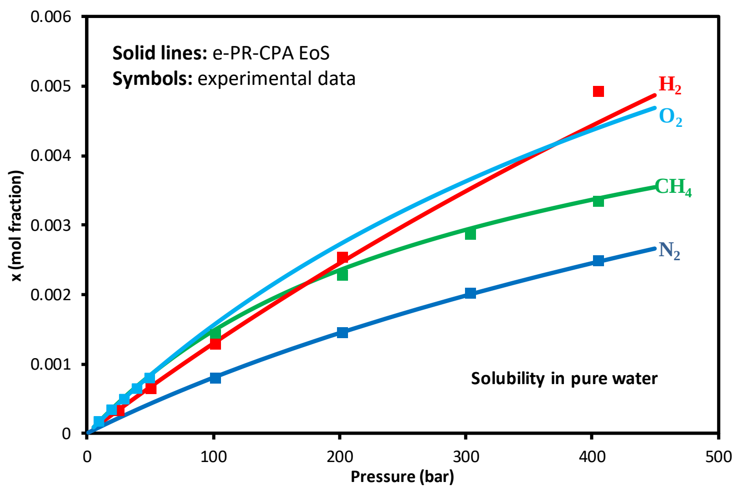
SOME COMMENTS...

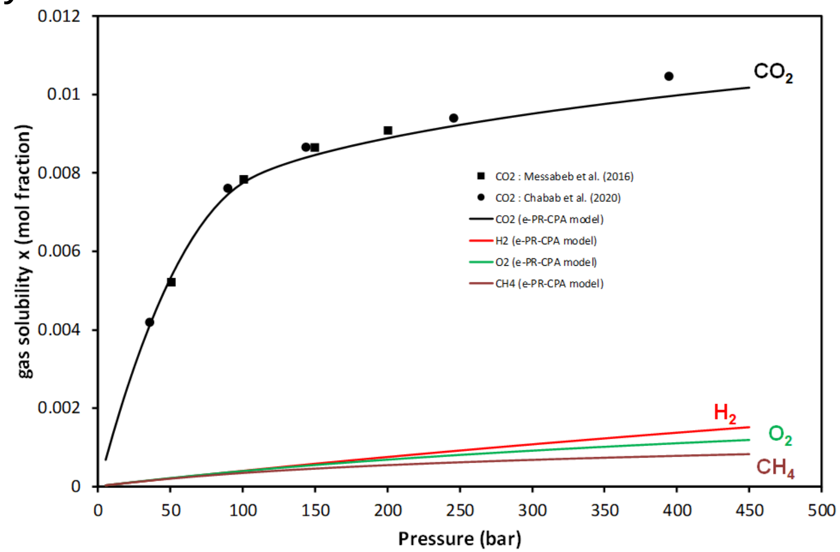
1) Salting-out effect of CH_4, N_2, O_2, and H_2 in 1m NaCl brine

	CH_4	O_2	N_2	H_2
$100*(1-x_{in\ brine}/x_{in\ water})$	25.35	25.38	25.24	**17.18 (This work)** 12.25 (Torín & Trusler 2021) 24.28 (Chabab et al. 2020)

2) Gas solubility dependencies:

- Intermolecular forces (HB, e.g. CO_2)
- Coulombic interactions
- Molecule size
- Polarizability



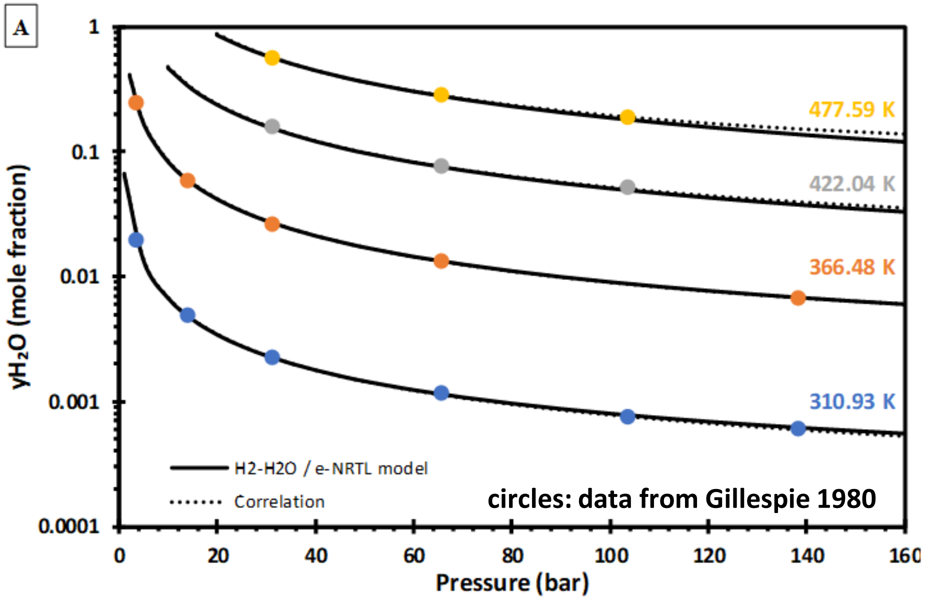


*(To go deeper, see **Battino, R., & Seybold, P. G. (2011). The O_2/N_2Ratio Gas Solubility Mystery.***

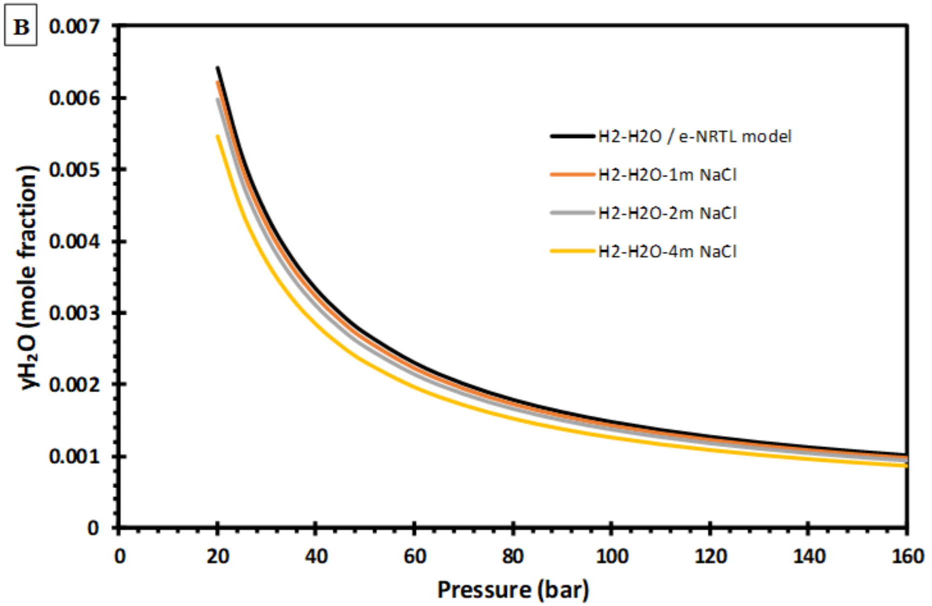
I.II. Thermodynamic modeling

b) Modeling results (vapor phase)

water content in H_2+H_2O system



water content in $H_2+H_2O+NaCl$ system



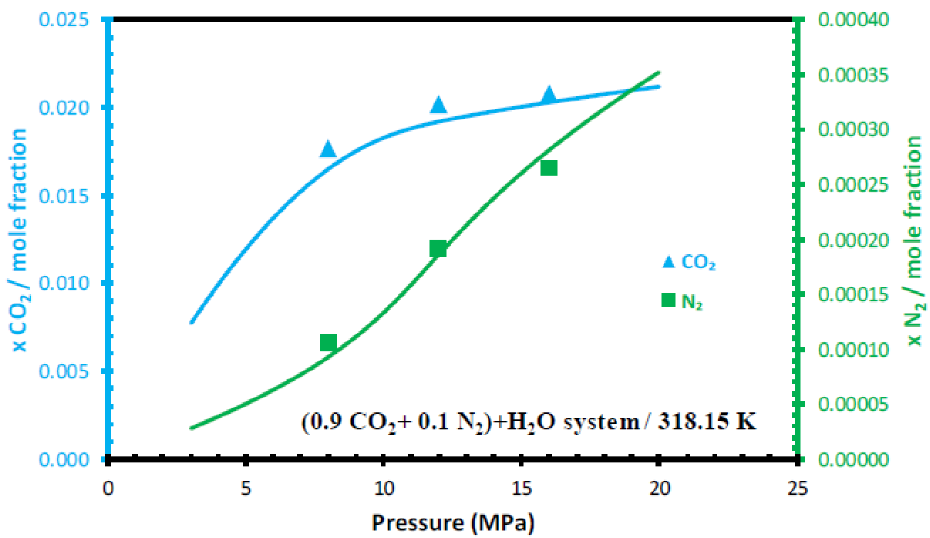
- ❑ Water content in the gas phase is well captured by the models
- ❑ The predictions of the eNRTL-PR model show that the presence of salt alone is not sufficient to achieve an acceptable moisture content (e.g. 5 ppm of H_2O(v) in H_2(g) for PEM fuel cells, ISO 14687-2:2012).

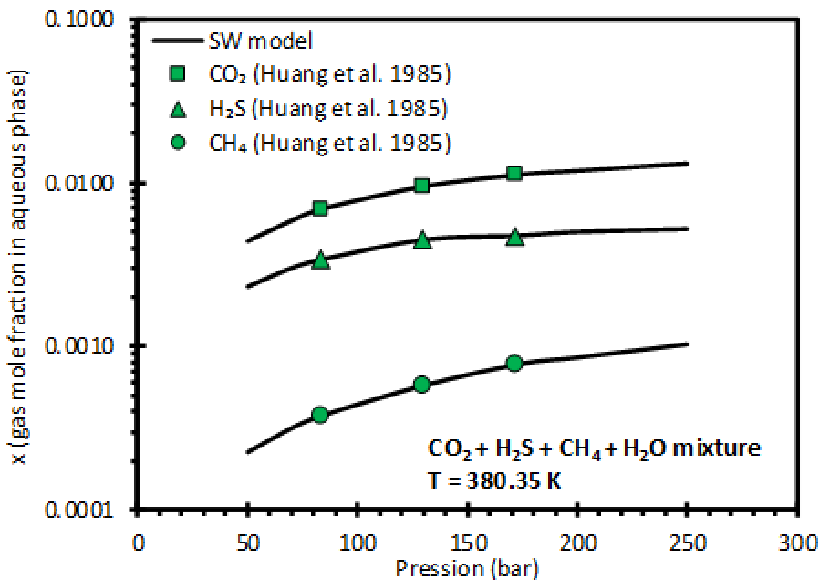
Part 1: Phase Behavior of H_2 mixtures for UHS

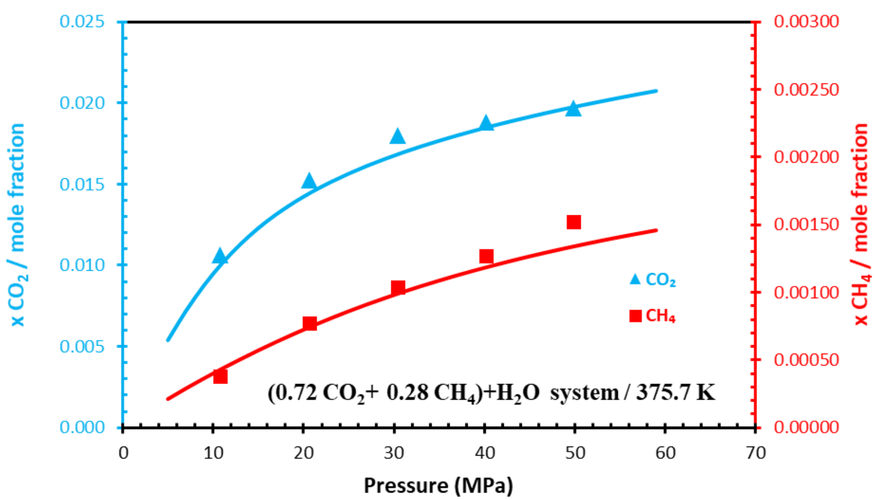
I.II. Thermodynamic modeling

Ref : 1) Chabab, S et al. (2021). Energies, 14, 5239.
2) Chabab, S et al. (2022). EGC 2022, Berlin.

c) solubility of gas mixtures in water



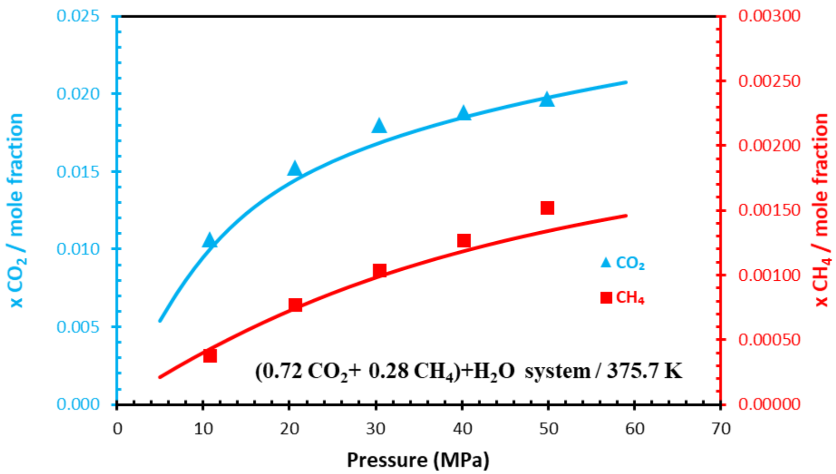


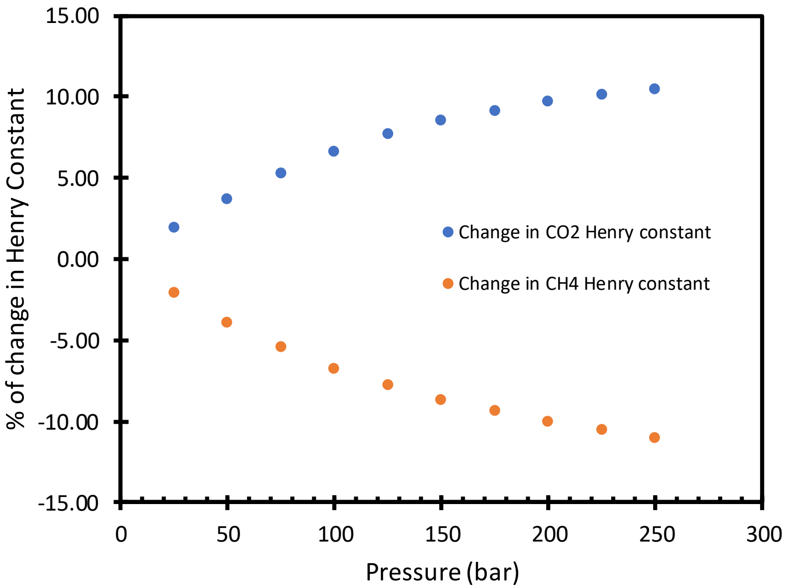


- No data available for H_2/gas mixtures in water and brine. (Work in progress)
- The model (SW EoS) predicts accurately the solubility of gas mixtures (CO_2, H_2S, CH_4, N_2)

I.II. Thermodynamic modeling

d) co-solubility effect (gas mixtures) ?





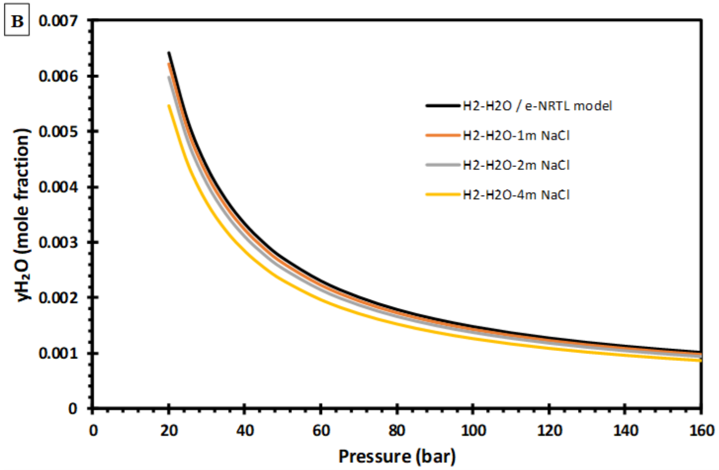
$$H_i = \lim_{x_i \to 0} \frac{f_i}{x_i} = \lim_{x_i \to 0} \frac{\varphi_i y_i P}{x_i}$$

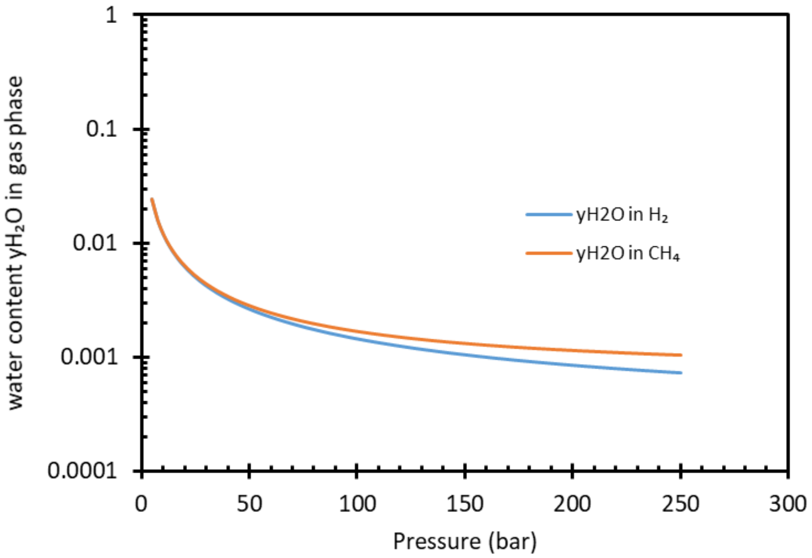
% of change = difference between apparent constant H (in the ternary system) and constant H (in the binary system)

Can we deduce that there is co-solubility in this case ?

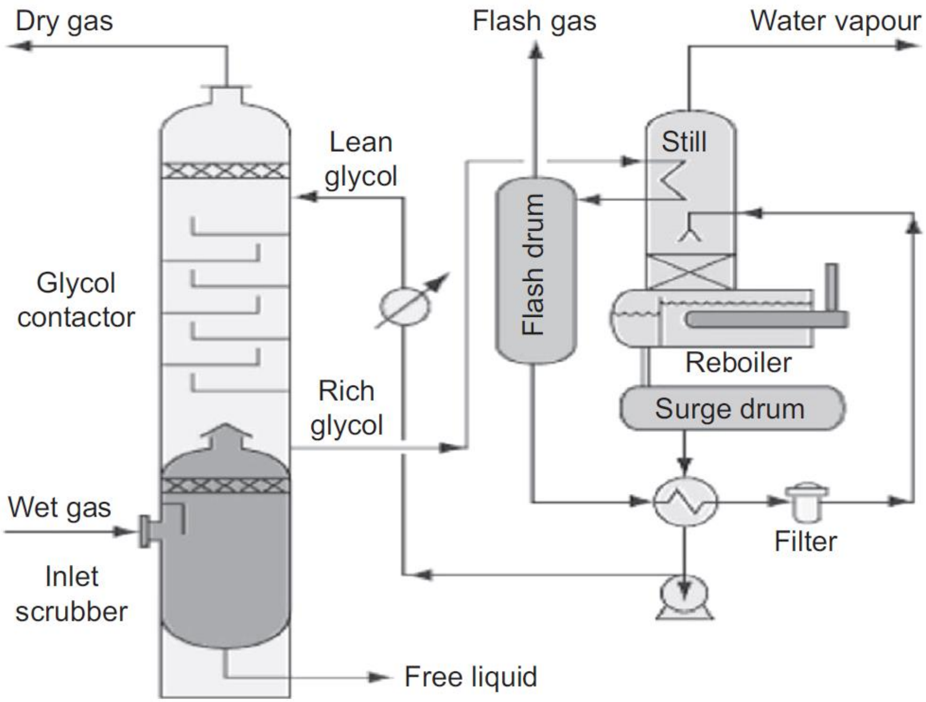
2) Implication on H_2 dehydration

PART 2: IMPLICATION ON H_2 DEHYDRATION

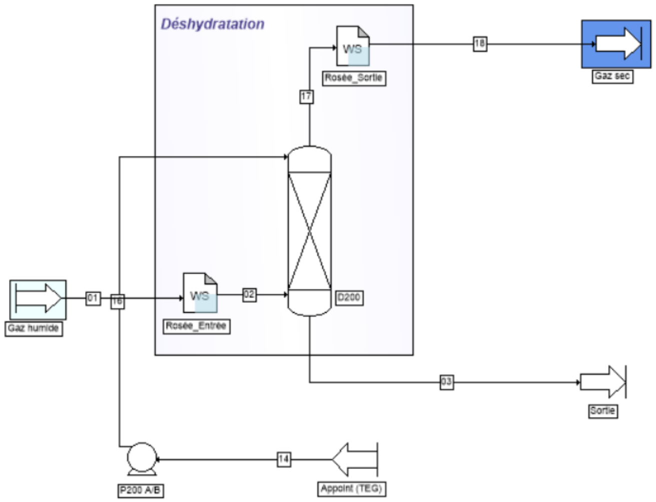


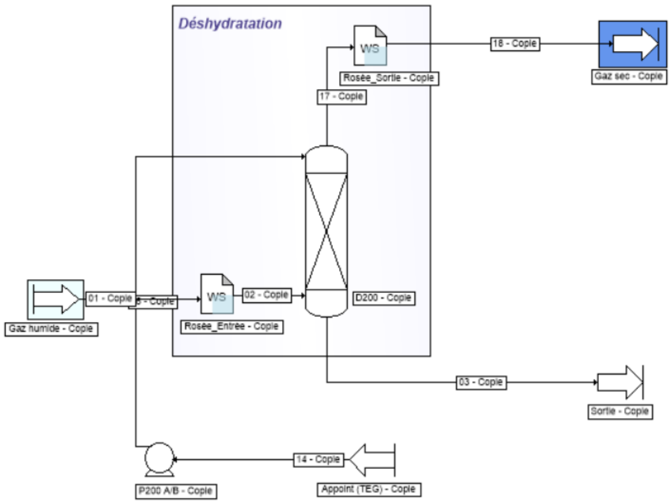


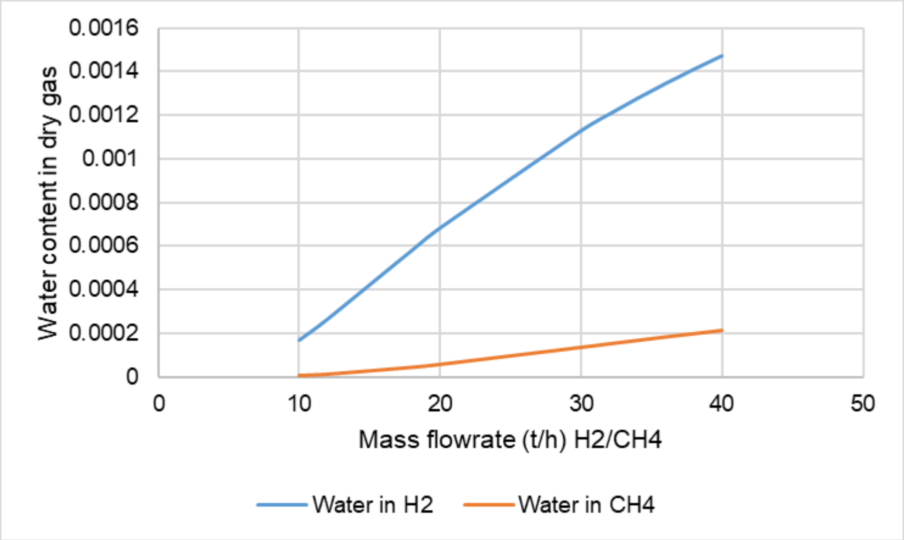
The process traditionally used for natural gas is TEG absorption

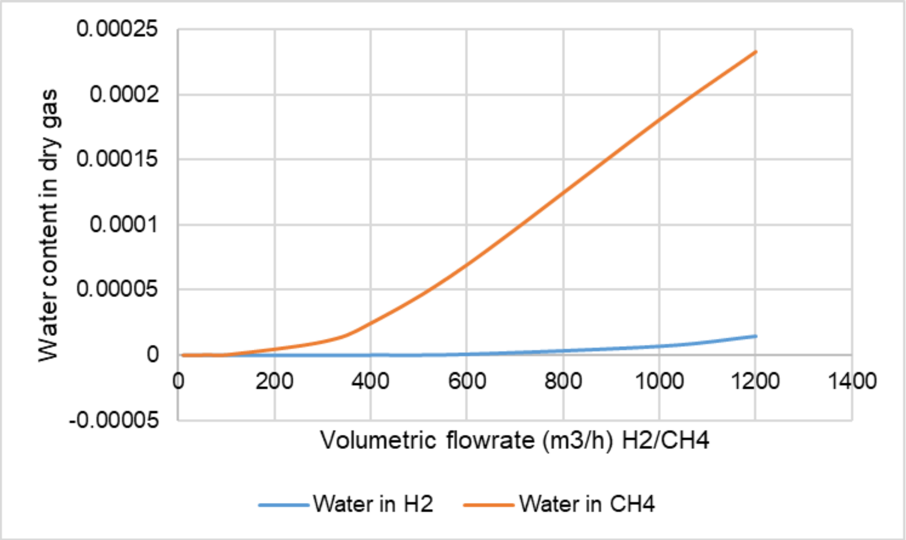


PART 2: IMPLICATION ON H_2 DEHYDRATION







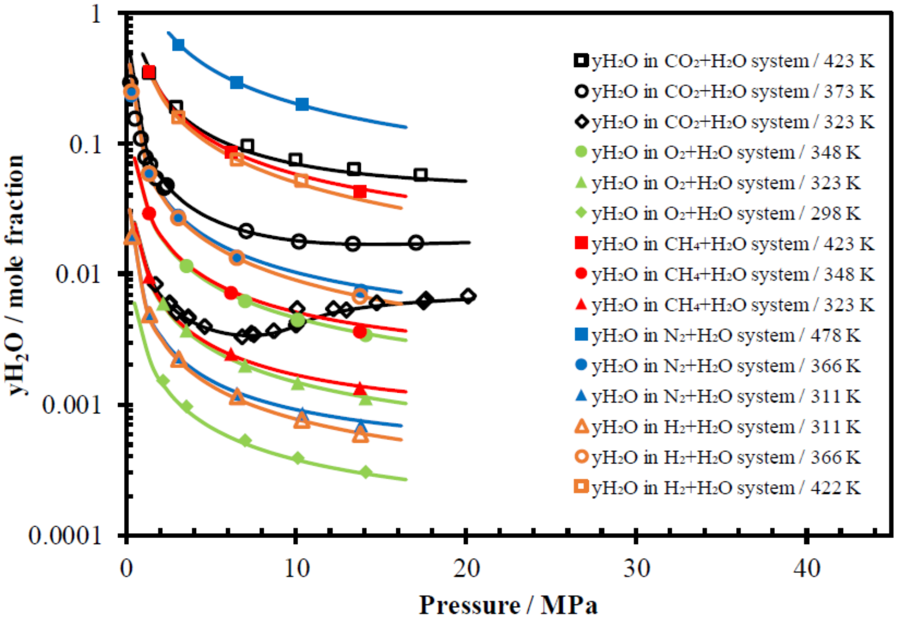


PART 2: IMPLICATION ON H_2 DEHYDRATION

Are the actual dehydration process adapted for H_2?

- In-depth study on extracted gas flow rate and impurity content
- Effect of stripping gas
- Column dimensions
- Solvent efficiency

…



Ref : Chabab, S et al. (2021). Energies, 14, 5239.

CONCLUSIONS

Summary

- ✓ Importance of thermophysical properties for UHS
- ✓ Reliability of the chosen technique in relation to the challenge (sparingly soluble gas)
- ✓ Effect of temperature, pressure and salinity on H_2 solubility and water content
- ✓ Data treatment with different models using different approaches
- ✓ Solubility of gas-mixtures and co-solubility effect

Perspectives

- ❑ Mixed-gas co-solubility (cushion gas, underground bio-methanation, etc.)
- ❑ Mixed-gas water content
- ❑ Transport properties

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