UNDERSTANDING FLUIDS THERMOPHYSICAL PROPERTIES FOR UNDERGROUND HYDROGEN STORAGE: EXPERIMENTAL AND COMPUTATIONAL INSIGHTS

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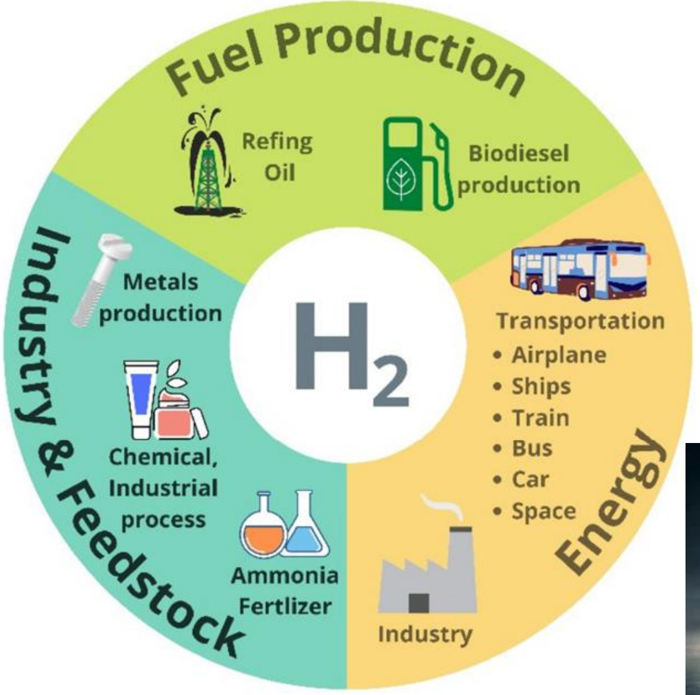
Colloque GdR HydroGEMM
Nov 2024

CONTEXT & MOTIVATIONS

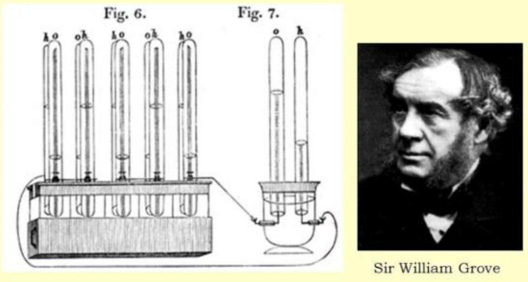
HYDROGEN: BACK TO THE FUTURE ?

A lot of potential

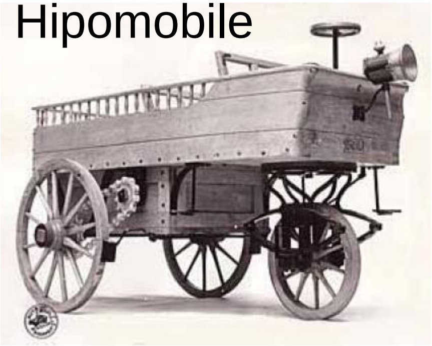


Not really new

1839: First Fuel Cell (Grove's "Gas Battery")



Sir William Grove



Hipomobile

BACK TO THE FUTURE

Increasing Hy-pe

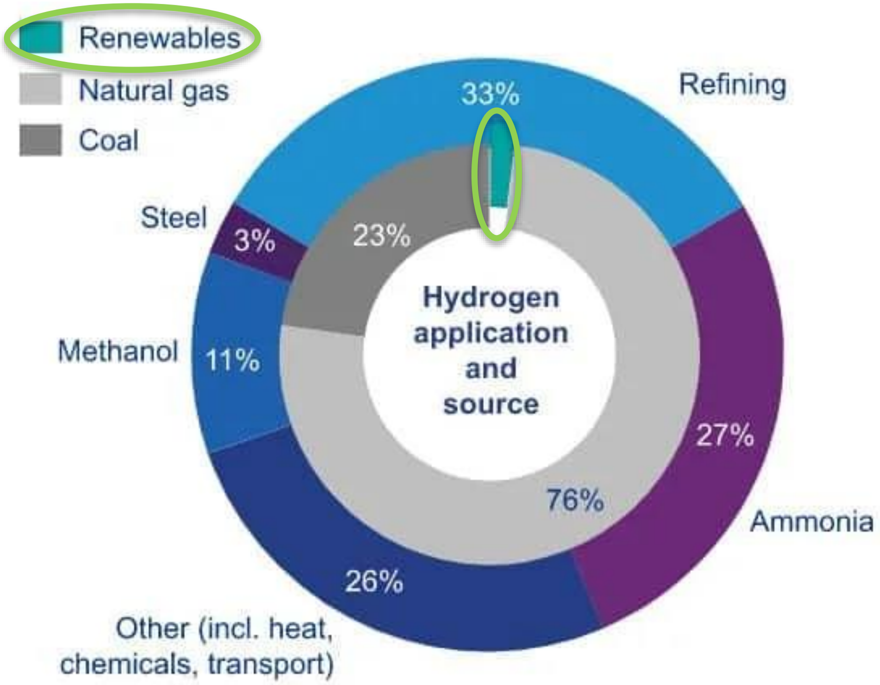
New Dolorean

Fébus

HYDROGEN: BACK TO THE FUTURE ?

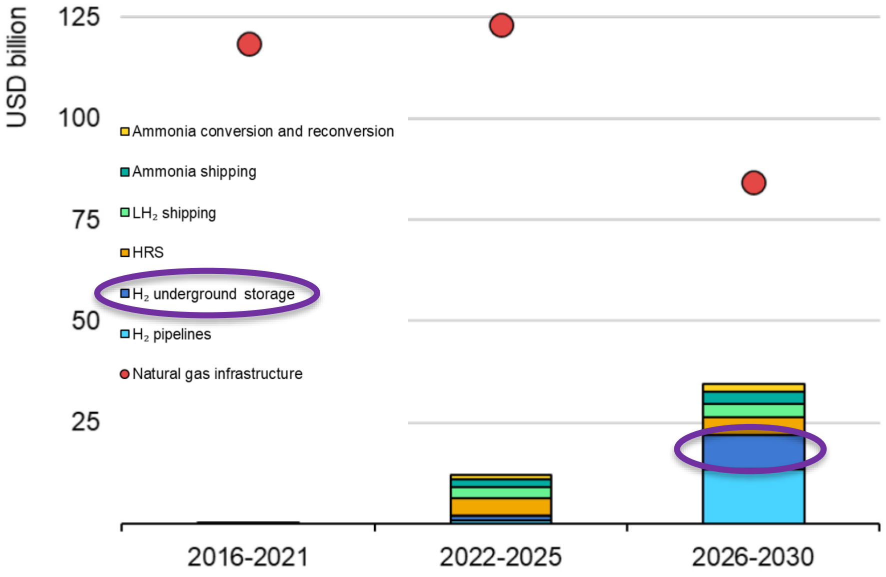
but…

Hydrogen use and source



https://carboncredits.com/

Global annual investment in gas/H2 infrastructure

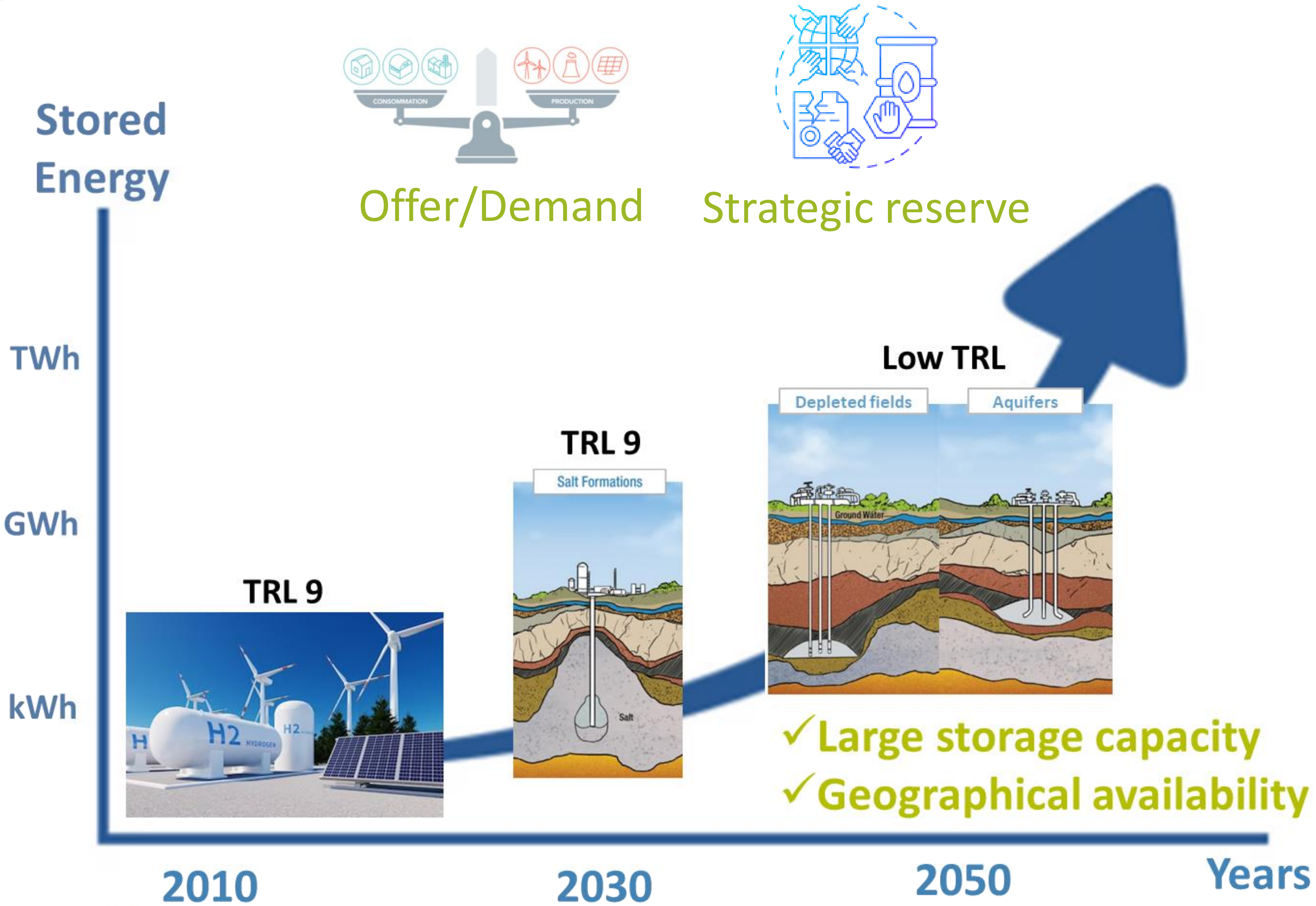


IEA, 2023

~100 Mt/y (~3 500 TWh/y)

~300 Mt/y (2050)

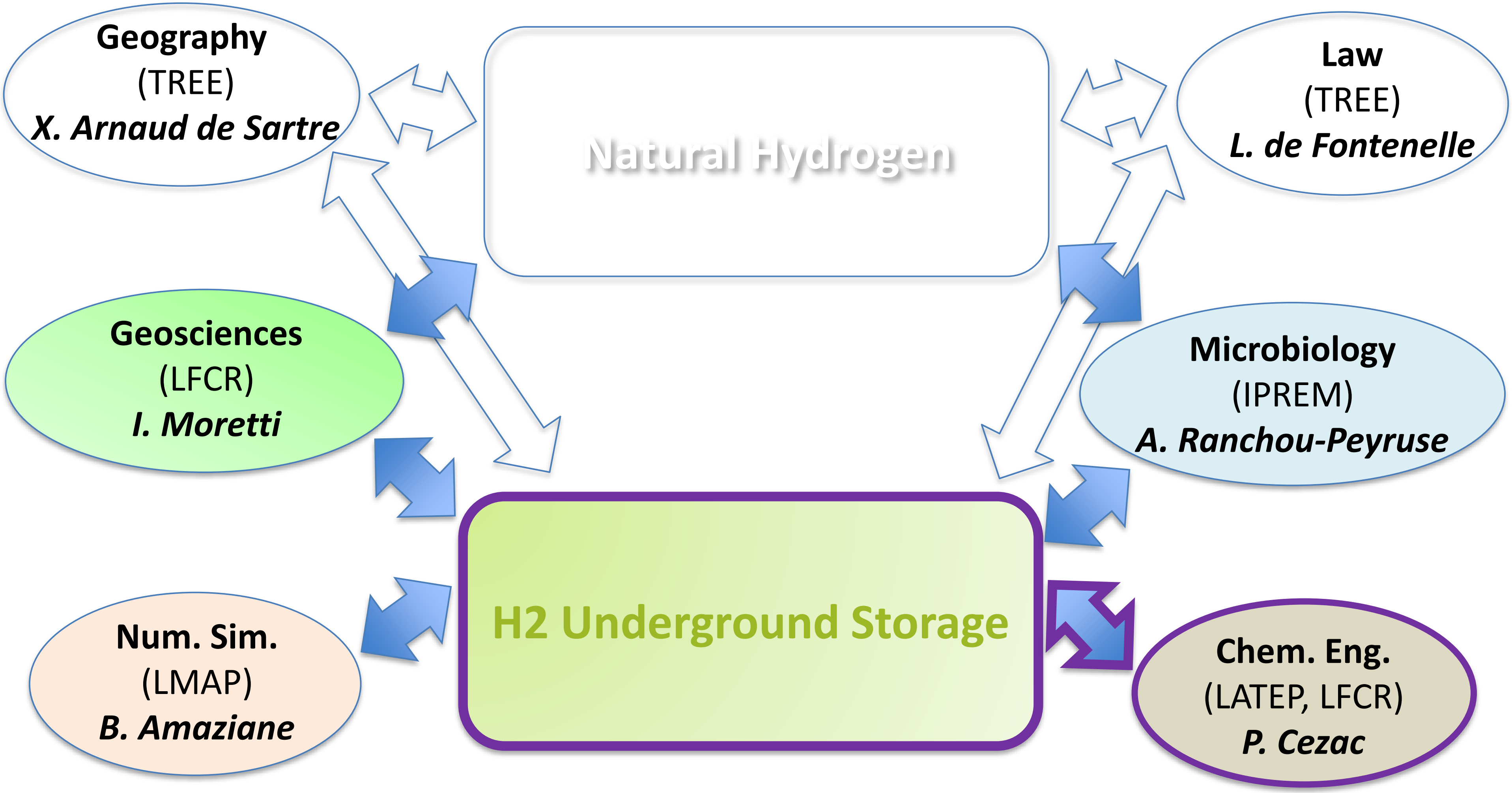
UNDERGROUND HYDROGEN STORAGE: THE FUTURE ?



- ✓ Large storage capacity
- ✓ Geographical availability

CONTEXT AT UPPA

UNDERGROUND H2 ACTIVITIES AT UPPA



Geography
(TREE)
X. Arnaud de Sartre

Natural Hydrogen

Law
(TREE)
L. de Fontenelle

Geosciences
(LFCR)
I. Moretti

Microbiology
(IPREM)
A. Ranchou-Peyruse

Num. Sim.
(LMAP)
B. Amaziane

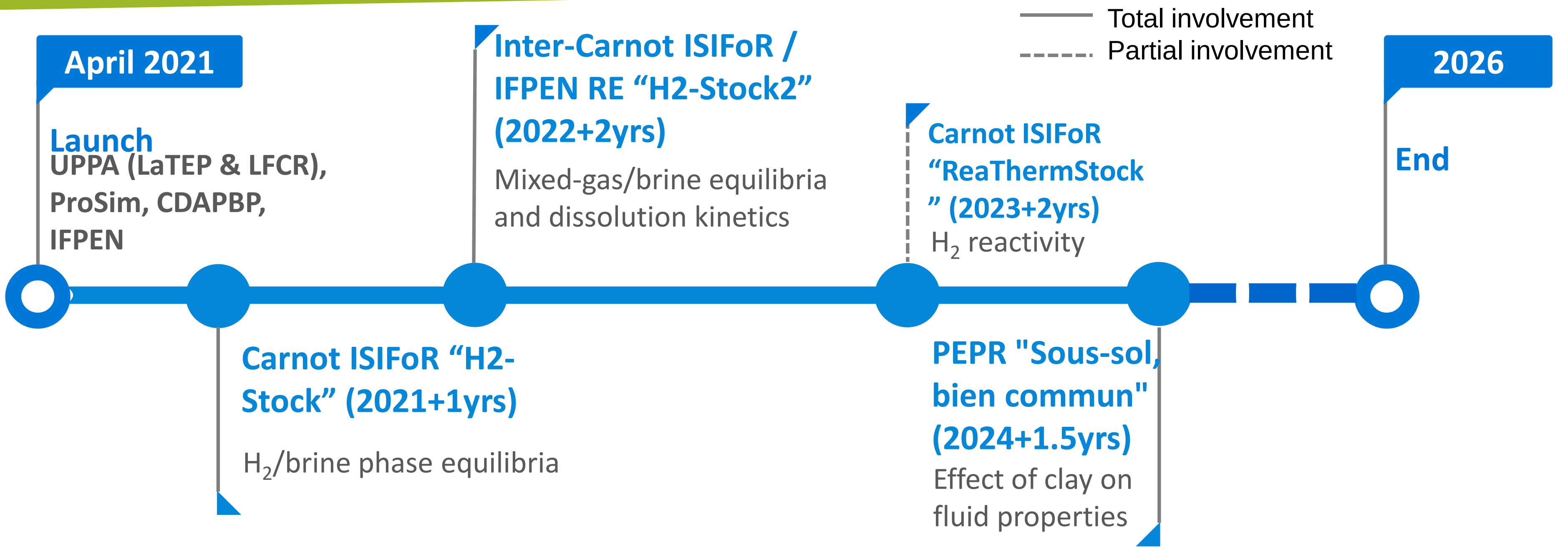
H2 Underground Storage

Chem. Eng.
(LATEP, LFCR)
P. Cezac

More than 40 UPPA researchers involved !

And many partners (Terega, Storengy, TotalEnergies, Prosim, IFPEN…)

THERMOPHYSICAL PROPERTIES: HYDR JUNIOR CHAIR



Total involvement

Partial involvement

April 2021

Launch

UPPA (LaTEP & LFCR), ProSim, CDAPBP, IFPEN

Carnot ISIFoR "H2-Stock" (2021+1yrs)

H_2/brine phase equilibria

Inter-Carnot ISIFoR / IFPEN RE "H2-Stock2" (2022+2yrs)

Mixed-gas/brine equilibria and dissolution kinetics

Carnot ISIFoR "ReaThermStock" (2023+2yrs)

H_2 reactivity

PEPR "Sous-sol, bien commun" (2024+1.5yrs)

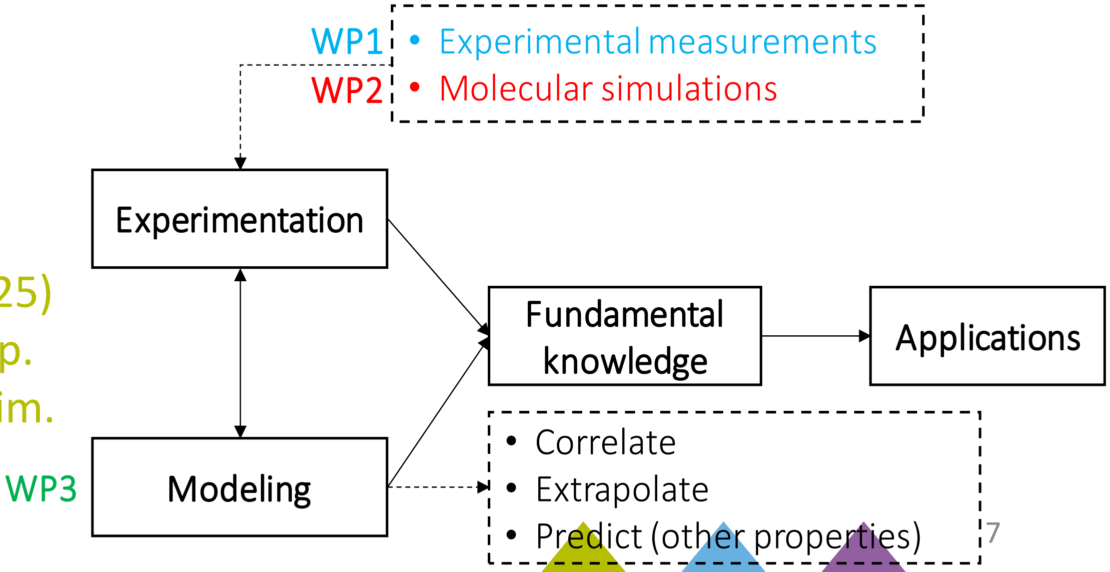
Effect of clay on fluid properties

2026

End

Research team

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



WP1
- Experimental measurements

WP2
- Molecular simulations

Experimentation

WP3

Modeling

Fundamental knowledge

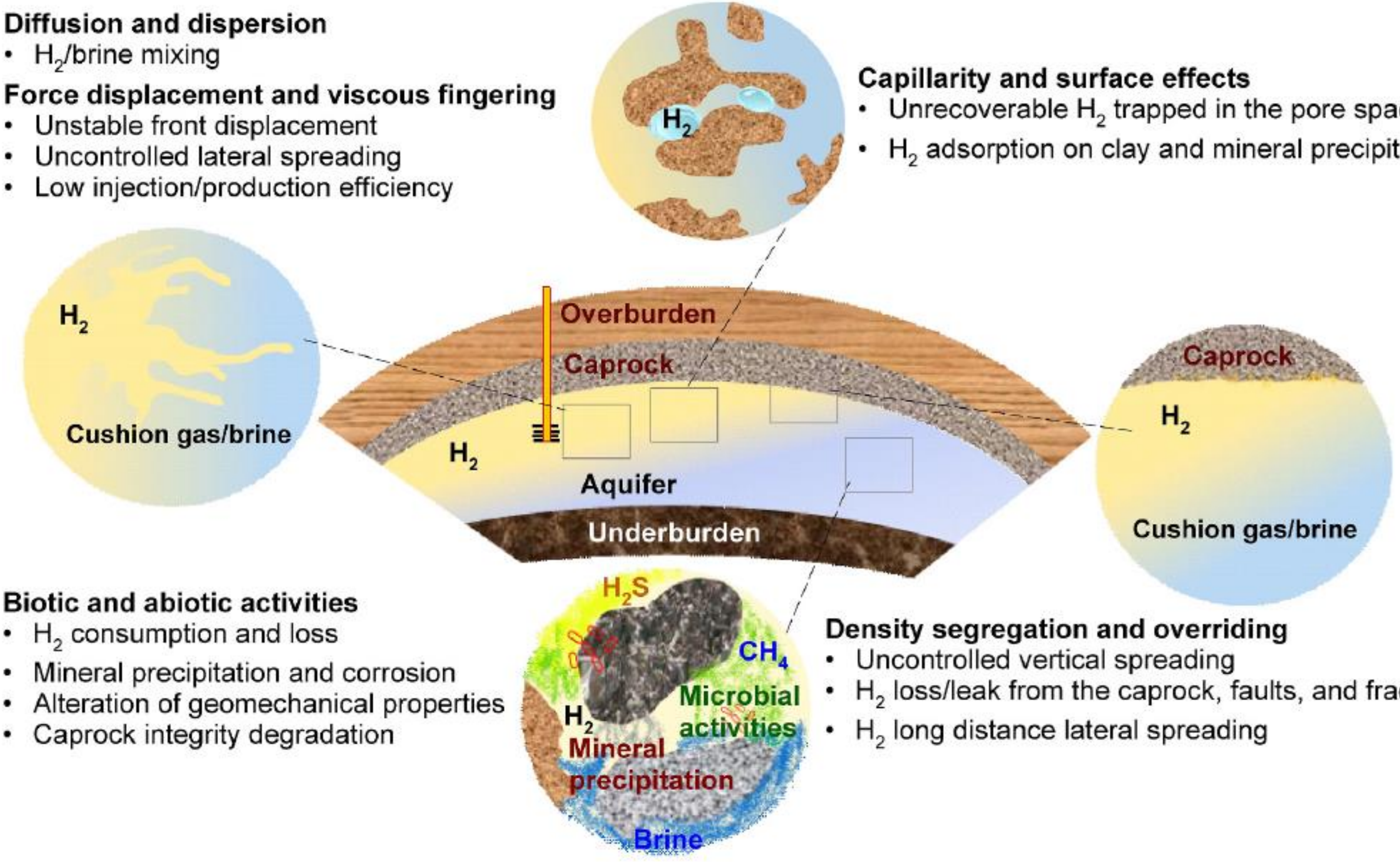
Applications

- Correlate
- Extrapolate
- Predict (other properties)

ISSUES

UHS IN AQUIFERS ISSUES

Raad et al. (2022)



Diffusion and dispersion

- H_2/brine mixing

Force displacement and viscous fingering

- Unstable front displacement
- Uncontrolled lateral spreading
- Low injection/production efficiency

Capillarity and surface effects

- Unrecoverable H_2 trapped in the pore spaces
- H_2 adsorption on clay and mineral precipitation

Biotic and abiotic activities

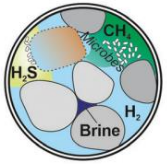
- H_2 consumption and loss
- Mineral precipitation and corrosion
- Alteration of geomechanical properties
- Caprock integrity degradation

Density segregation and overriding

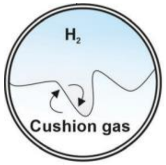
- Uncontrolled vertical spreading
- H_2 loss/leak from the caprock, faults, and fractures
- H_2 long distance lateral spreading

Gas (&Nuclear waste) storage knowledge….

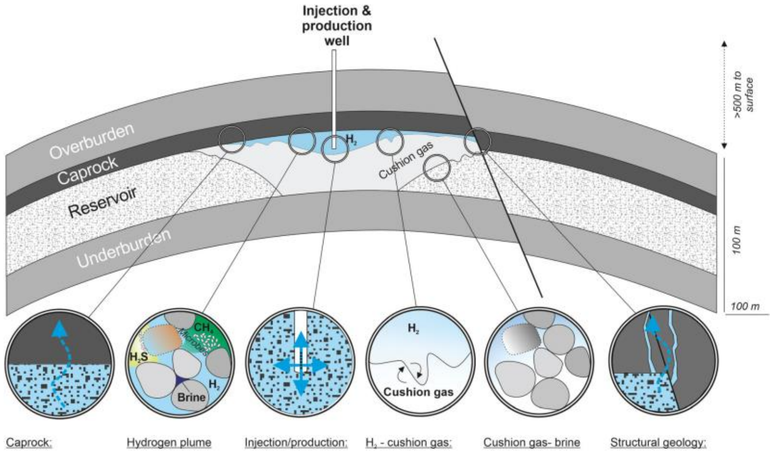
ISSUES PARTIALY DEALT WITH IN OUR TEAM



- ✓ **Loss through H_2 dissolution and (biogeochemical) reactivity**
- ✓ Potential mixing between H_2 and cushion gas



- ✓ **Sealing capacity of caprock**
- ✓ *Gas humidification*

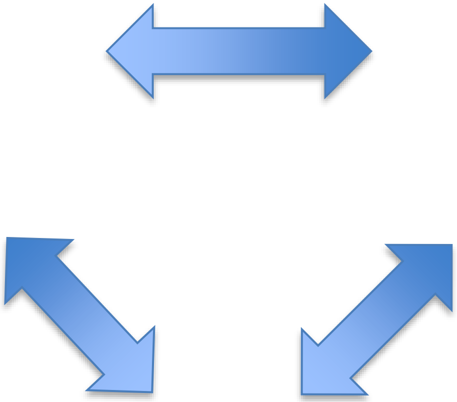


Fluid (H_2+Brine) **Thermophysical properties**

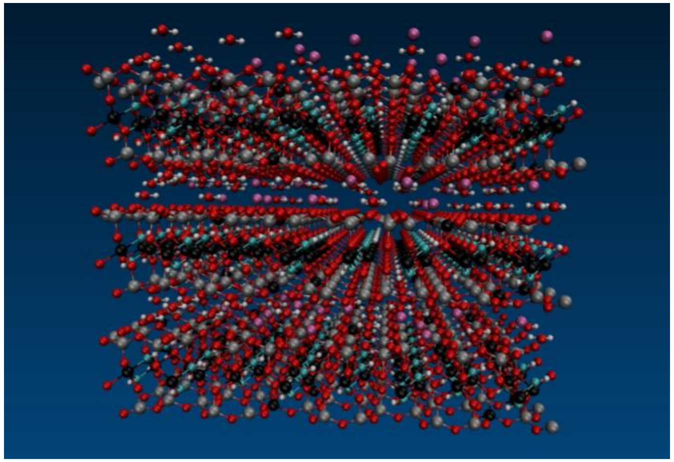
Density, solubility, diffusion…

METHODOLOGY

COMBINED APPROACHES

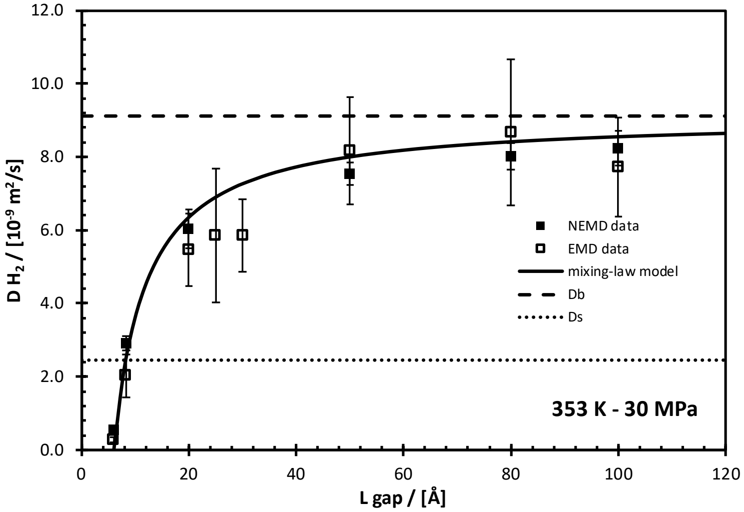


Molecular Simulations

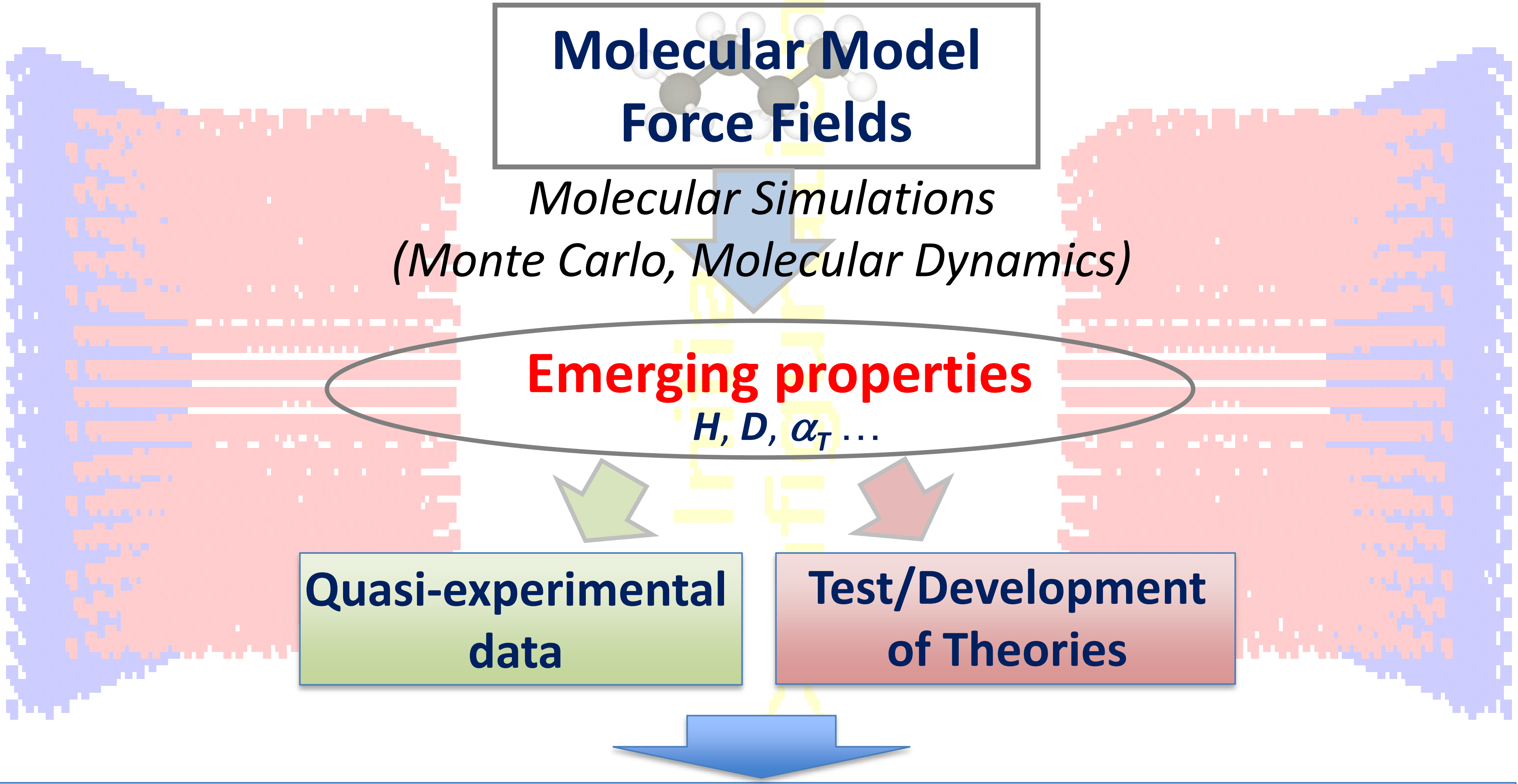


Experiments

Modeling



MOLECULAR SIMULATIONS



Molecular Model
Force Fields

Molecular Simulations
(Monte Carlo, Molecular Dynamics)

Emerging properties
$H, D, \alpha_T \ldots$

Quasi-experimental data

Test/Development of Theories

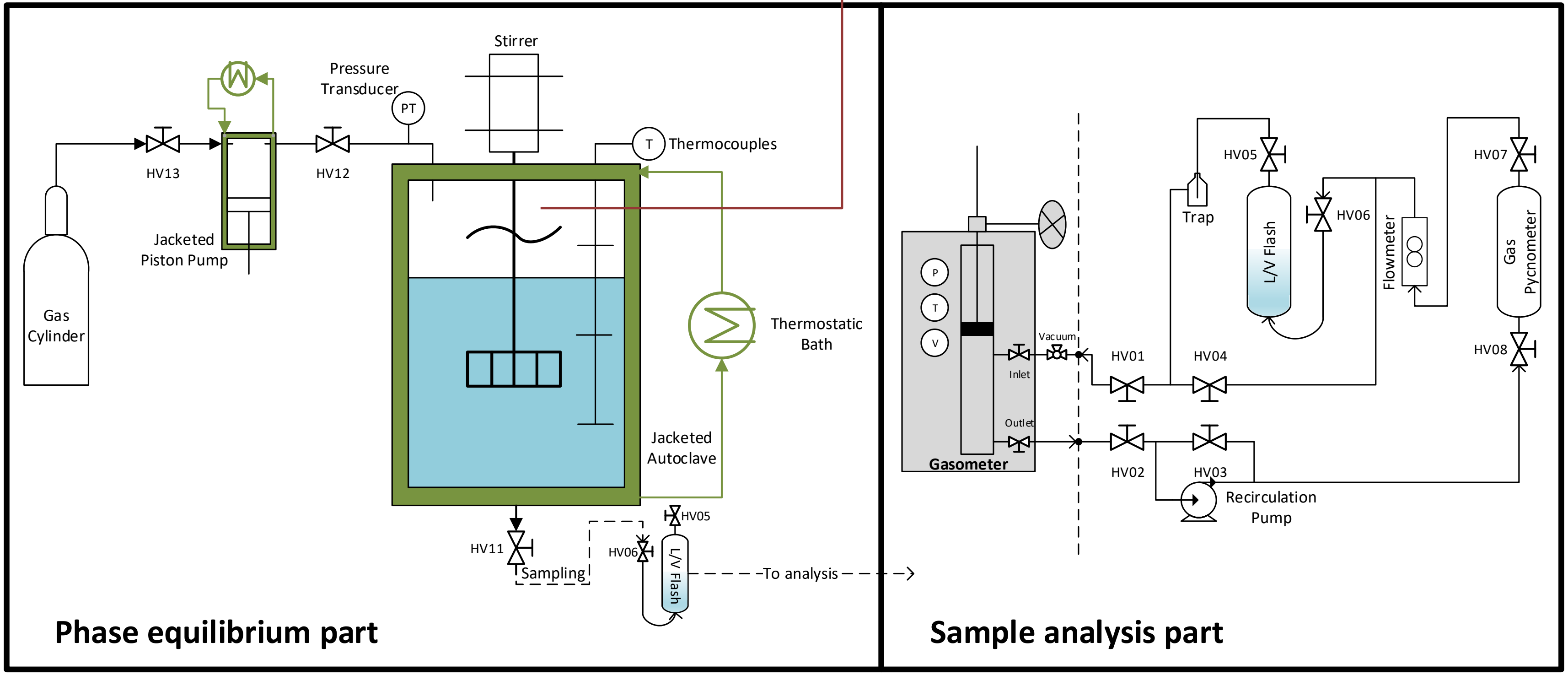
Exact results for a given molecular model …

But having good force fields is sometimes difficult…

EXPERIMENTS

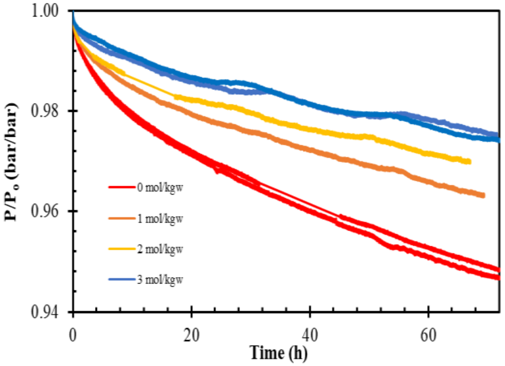
Solubility : Phase sampling

+ GC & KF titration



Chabab et al. (2024)

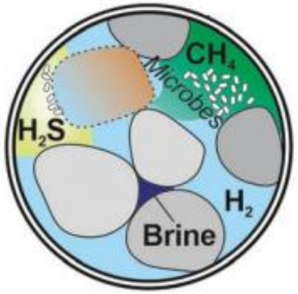
Diffusion : Pressure decay



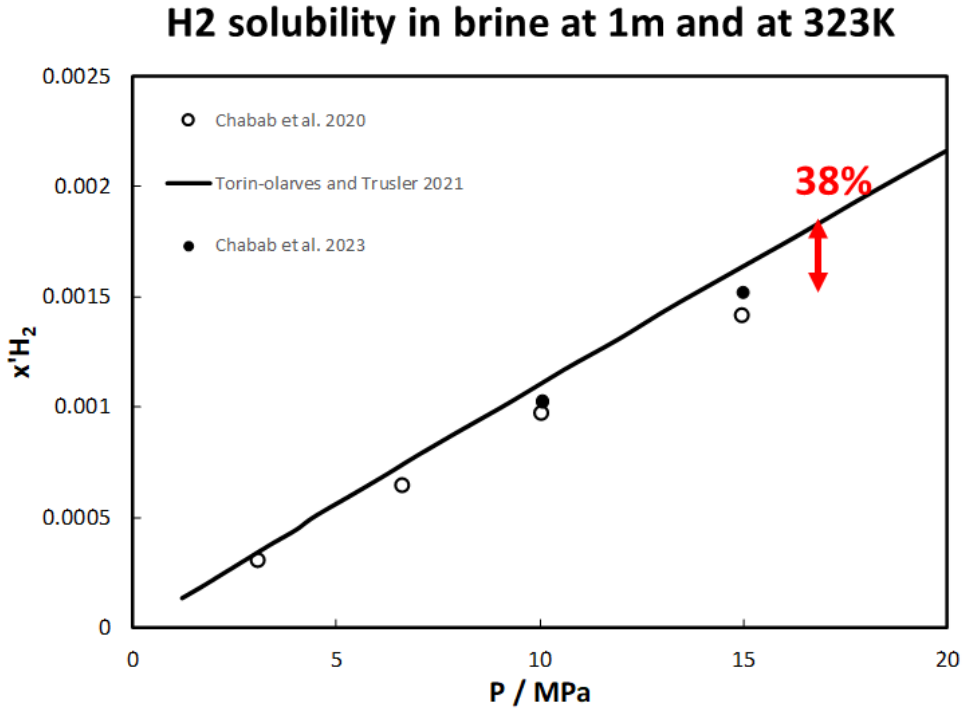
HYDROGEN SOLUBILITY IN BRINE

ISSUES

Low solubility of H_2 in brine
(~/10 CH_4 or ~/500 CO_2 in %mass)
No density driven phenomena
but



Lack of Data in Brine under UHS conditions
&
Discrepancy between data



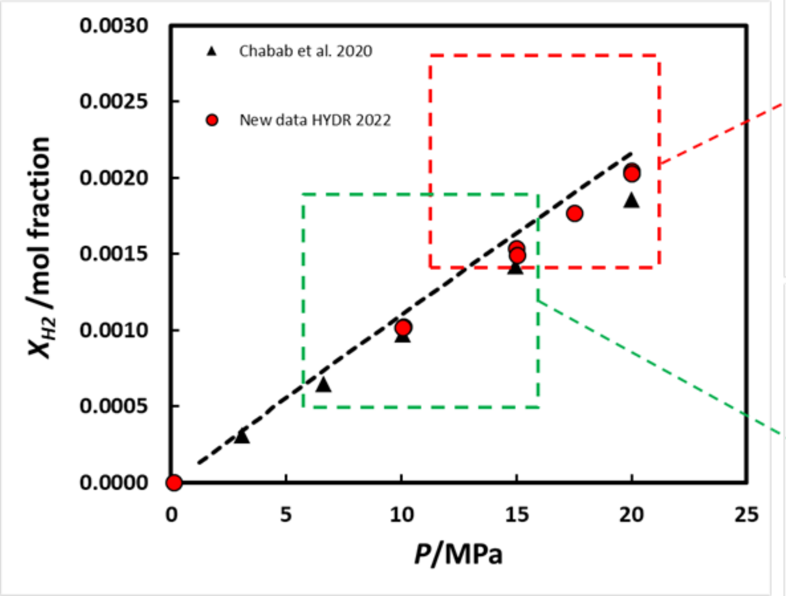
Needs of new data + thermodynamic modeling

EXPERIMENTAL RESULTS IN NACL BRINE

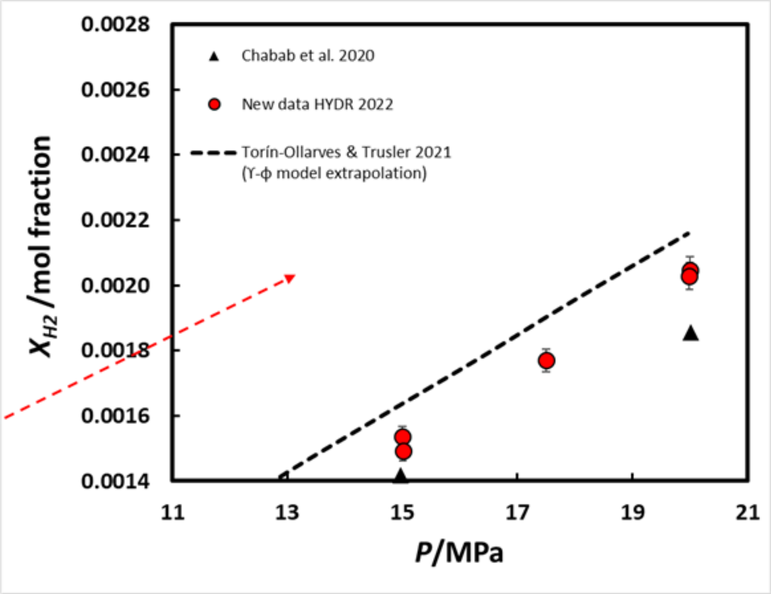
T = 298 - 373K, *P* up to 200 bar

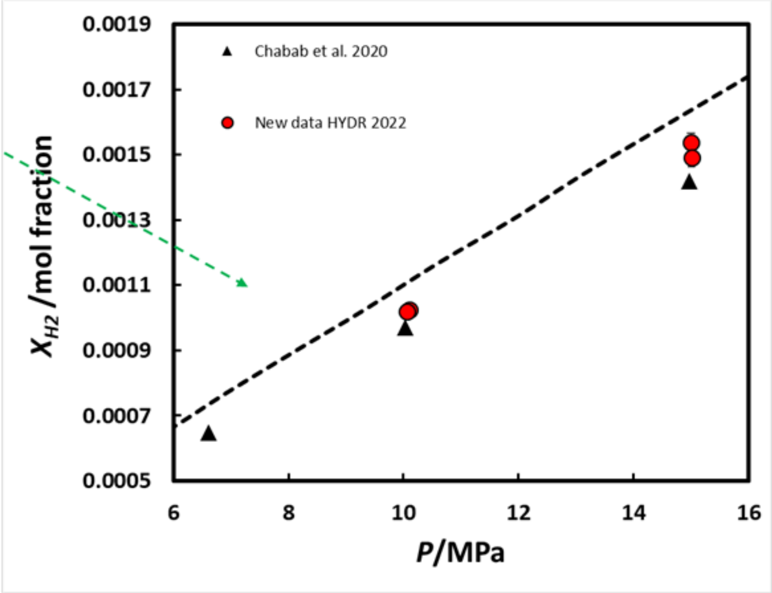
NaCl molality up to 4m

H2 solubility in brine at 1m and at 323K



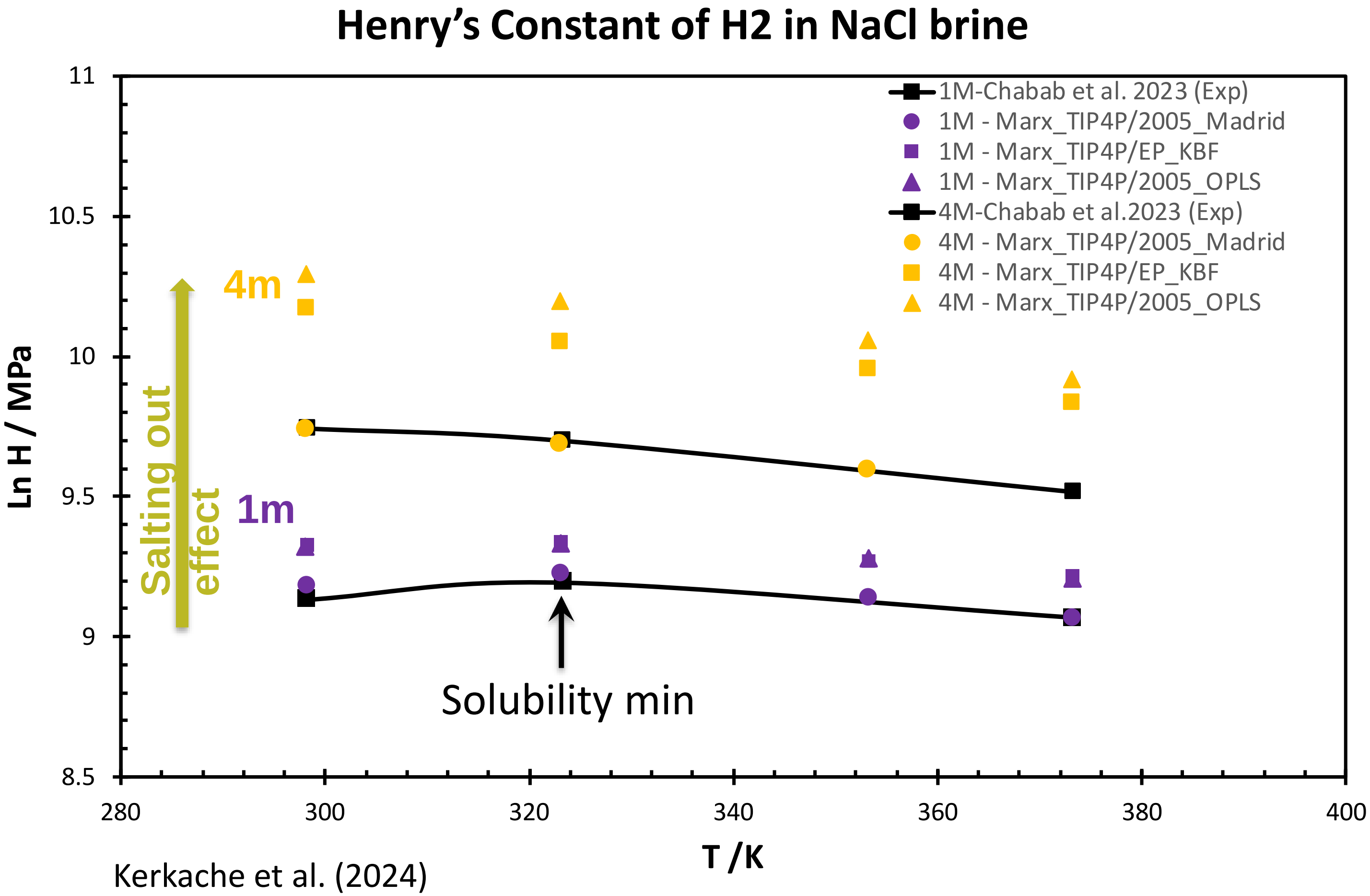
Chabab et al. (2024)





- ✓ **New data** between existing data
- ✓ **Lower salting-out** than Chabab 2020

MOLECULAR SIMULATIONS RESULTS IN NACL BRINE

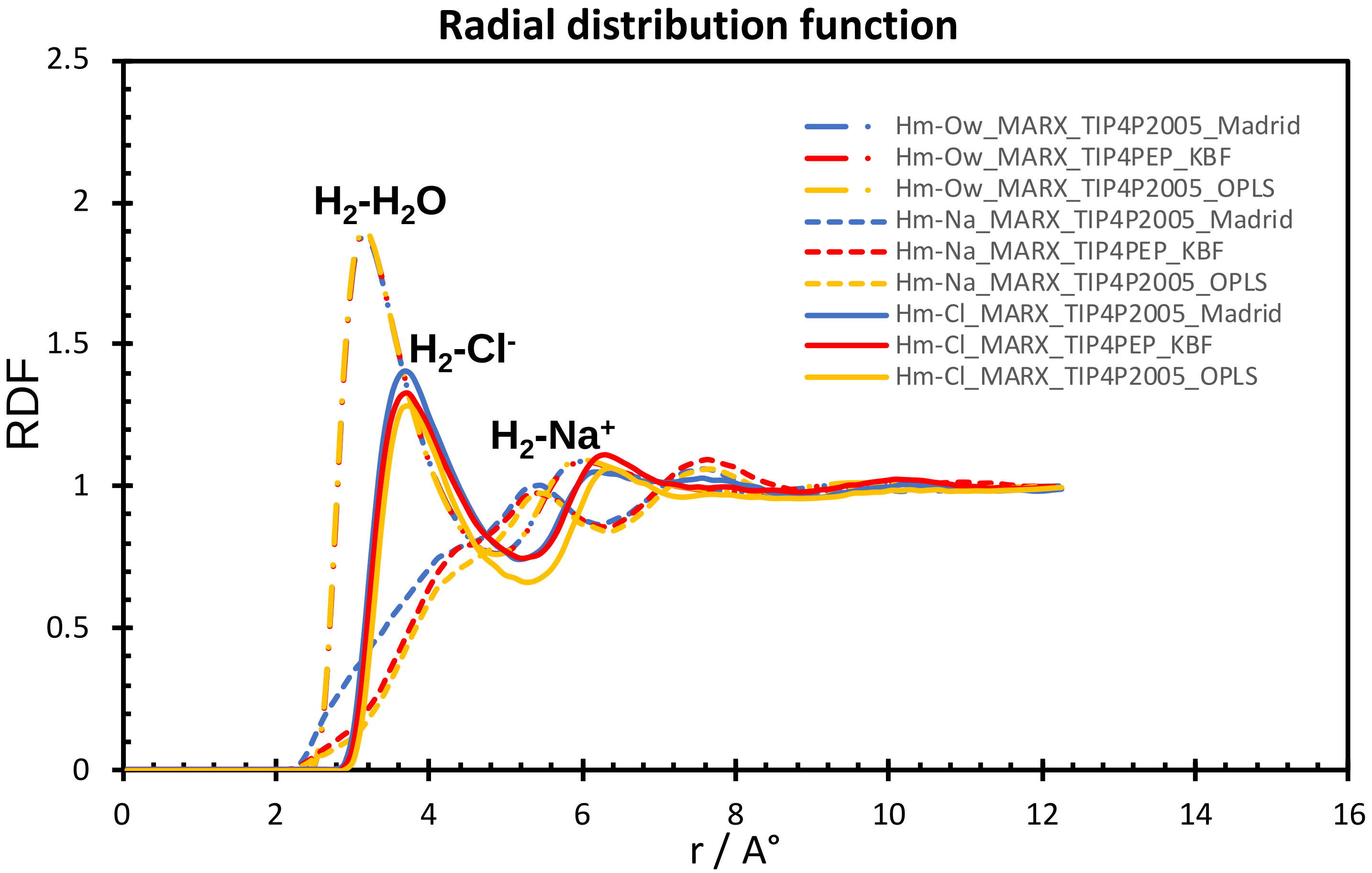


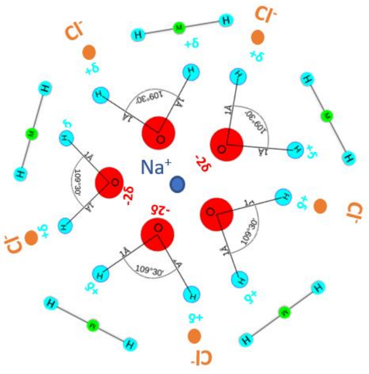
Kerkache et al. (2024)

$$x_i = \frac{f_i}{H_i}$$

- ✓ **Results** strongly **depend** on the **force fields…**
- ✓ **Marx-TIP4P/2005-Madrid** yields very **good results (AAD= 4%)**

MICROSCOPIC RESULT ANALYSIS





- ✓ **RDF** allows to **scrutinize** the **microscopic structure**
- ✓ **H2-H2O and H2-Cl- interactions are dominant!**

THERMODYNAMIC MODELING: ASYMETRIC APPROACH

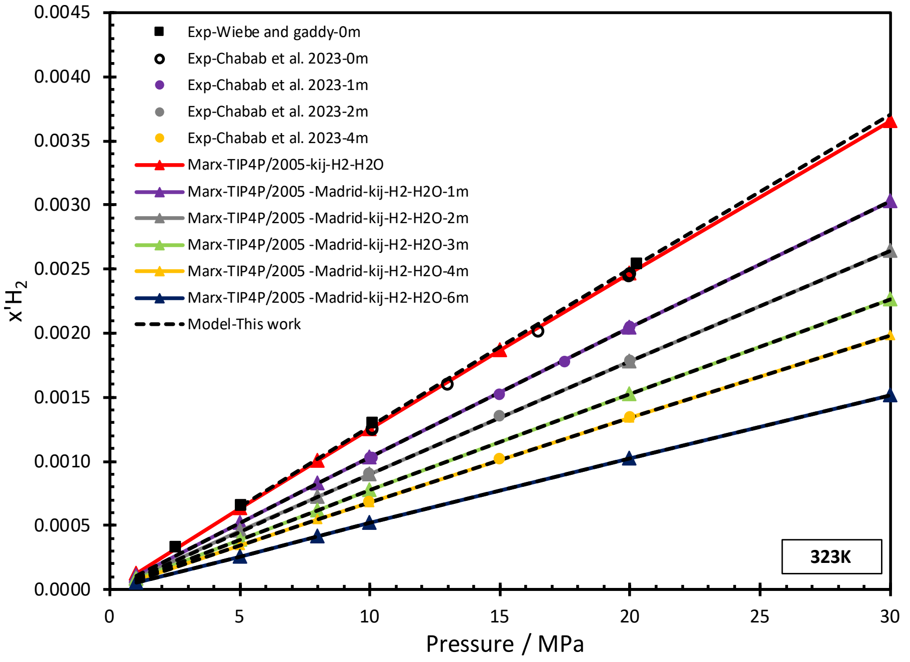
$$x_{H2}(\mathrm{T},\mathrm{P},m_s) = \frac{y_{H2}\cdot P\cdot \varphi_{H2}}{\underbrace{H_{H2}(T,P_w^{sat})}_{\text{Henry } H_2/H_2O}\cdot \gamma_{H2}\cdot \exp\left(\frac{\vartheta^{\infty}_{H2,w}}{RT}(P-P_w^{sat})\right)}$$

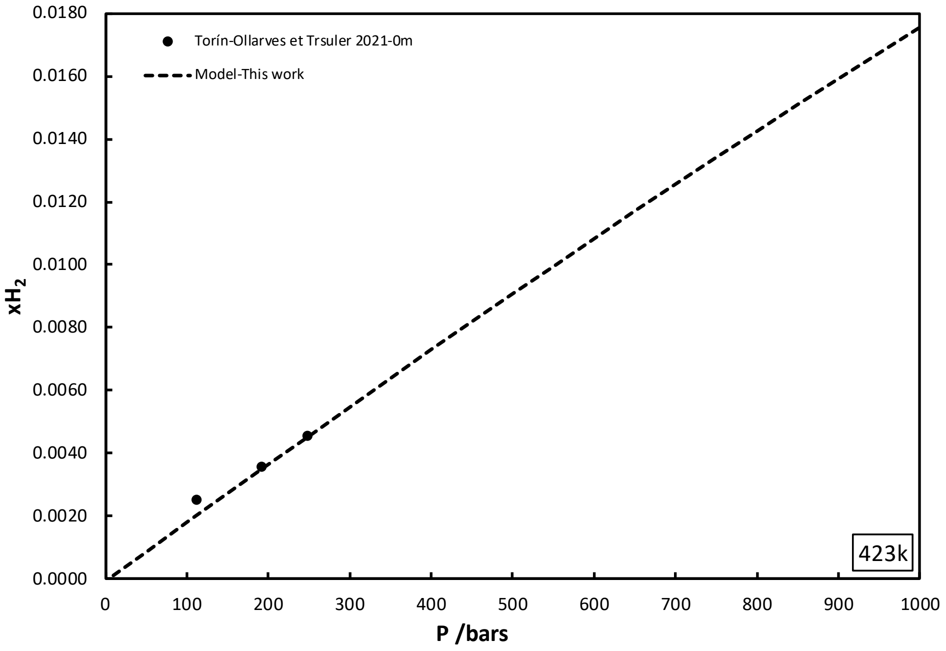
EoS

Poynting correction

$$\gamma_{H_2} = \ exp\ (K_s\, m_s)$$

$$Ks(kg\ .\ mol^{-1}) = A_0T + \frac{A_1}{T} + A_2\frac{T}{m_s} + A_3 + A_4 m_s\, T$$





- ✓ **Accurate results for H_2 solubility in brine** (T = 298 - 453 K, P up to 1000 bar and NaCl up to 6 mol NaCl/kg water).

HYDROGEN DIFFUSION IN BRINE

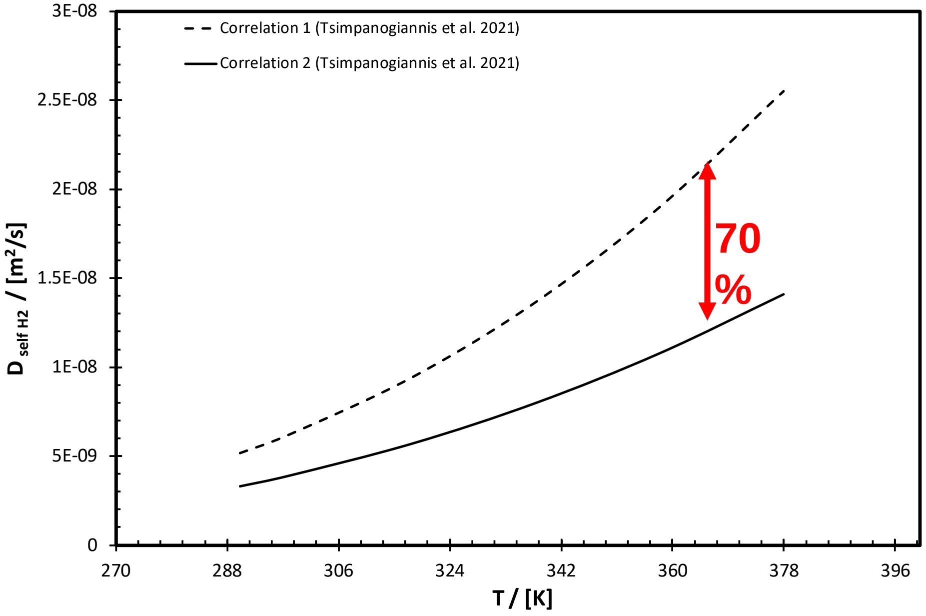
With C. Nieto-Drahi, Antoine Geoffroy-Neveux (IFPEN)

ISSUES

Kinetics of H_2 dissolution and mixing/leakage due to diffusion

($\sim$ x3 CH_4/CO_2)

but



H_2 diffusion in water at P= 1-10bar

Discrepancy between data

&

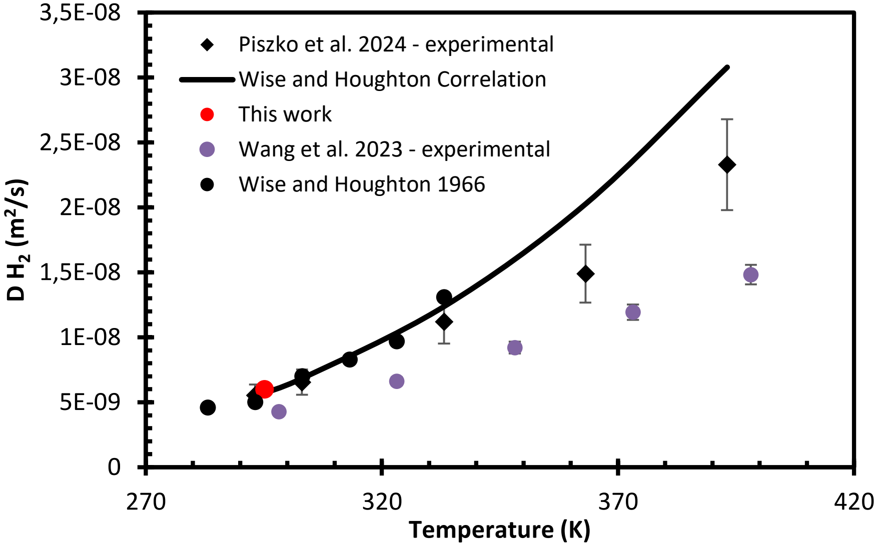
One exp. dataset in brine (Piszko et al. 2024)

Needs of new data + modeling

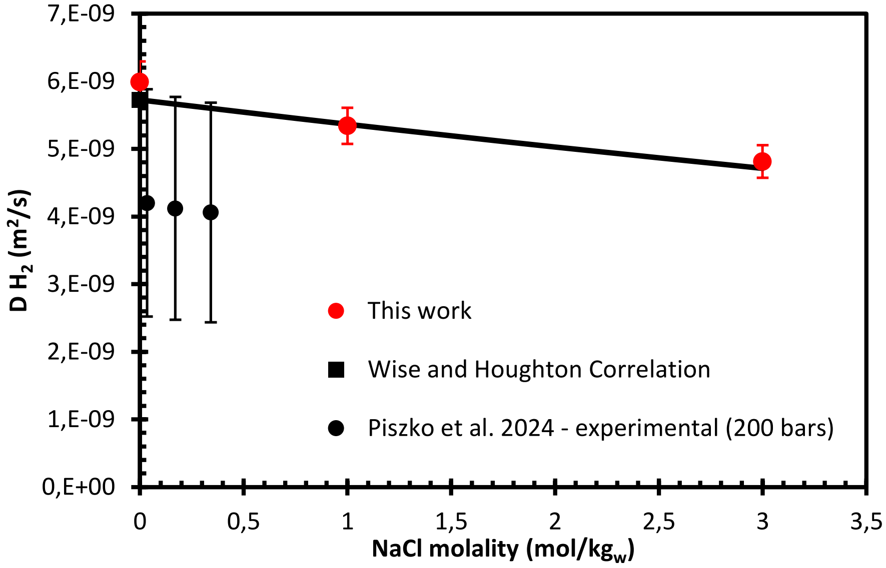
EXPERIMENTAL RESULTS IN NACL BRINE

T = 295K, *P* = 10 - 100 bar, NaCl molality up to 3m

H2 diffusion in water at low *pressure*



H2 diffusion in brine



De Souza Burti et al., in preparation

- ✓ **New data** in Brine using pressure decay
- ✓ **Difficulties to measure at high temperature**

RESULTS ANALYSIS IN NACL BRINE: EXCESS ENTROPY

$D \propto$ with $\exp(S_{H2})$

$$s_{\mathrm{H}_2} = -\frac{1}{2}\sum 4\pi r^2 \rho_\nu \int \{ g_{\mathrm{H}_2-\nu}(r) \ln g_{\mathrm{H}_2-\nu}(r) - [g_{\mathrm{H}_2-\nu}(r) - 1] \} dr$$

T

P

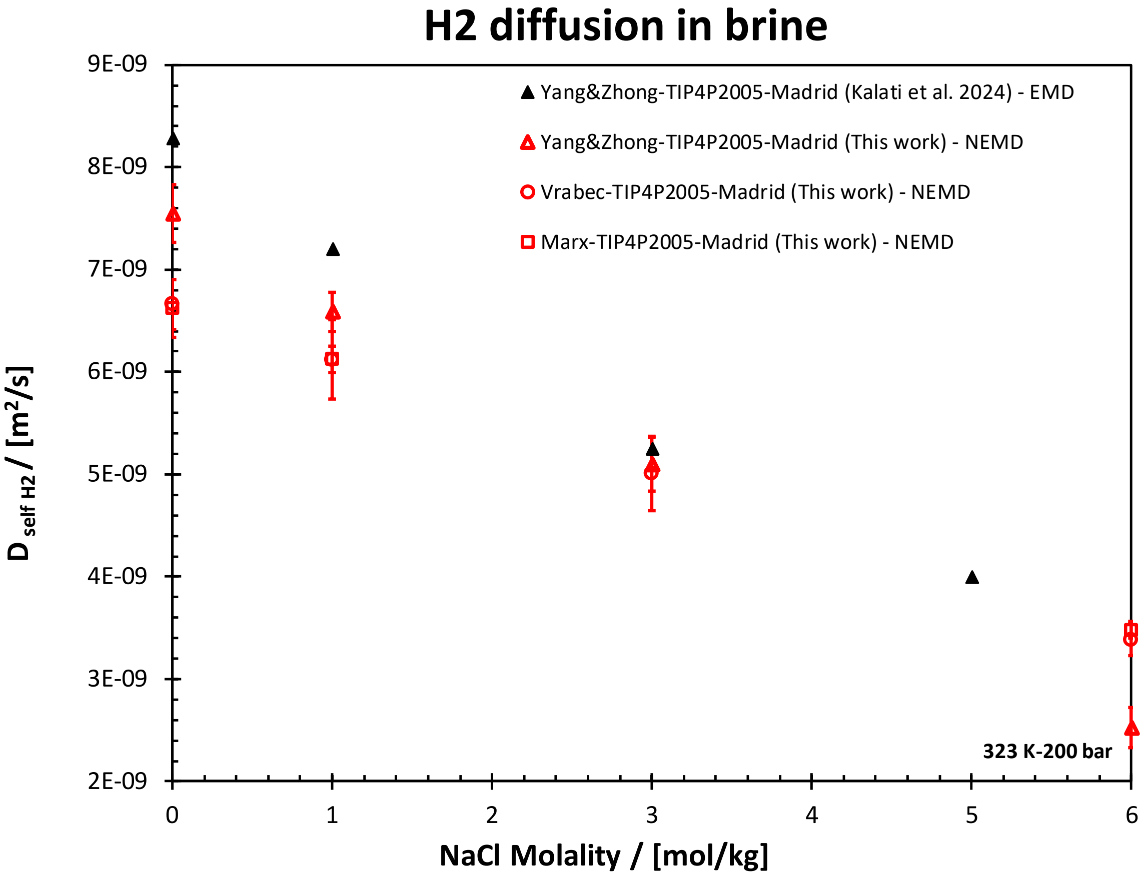
m_{NaCl}

	FF	Marx_TIP4P/2005_MadridTransport			
		S_{H_2}		D_{H_2} [m²/s]	
	Effect of Temperature				
↓	m=1, T=373K and P=200 bar	-1.584	↓	1.19E-08	↓
+	m=1, T=423K and P=200 bar	-1.400	+	1.92E-08	+
	m=1, T=473K and P=200 bar	-1.240		2.82E-08	
	Effect of Pressure				
+ ↓	m=1, T=323K and P=600 bar	-1.881	↓ −	6.00E-09	↓ −
	m=1, T=323K and P=1000 bar	-1.943		5.74E-09	
	Effect of molality				
↓	m=1, T=323K and P=200 bar	-1.817	↓	6.09E-09	↓
+	m=3, T=323K and P=200 bar	-1.885	−	5.36E-09	−
	m=6, T=323K and P=200 bar	-1.962		4.25E-09	

✓ **Excess entropy** allows to **decompose contributions to diffusion**

MOLECULAR SIMULATIONS RESULTS IN NACL BRINE

T = 298 - 373K, *P* up to 200 bar, NaCl molality up to 4m



Non-Equilibrium Molecular Dynamics to improve the statistics

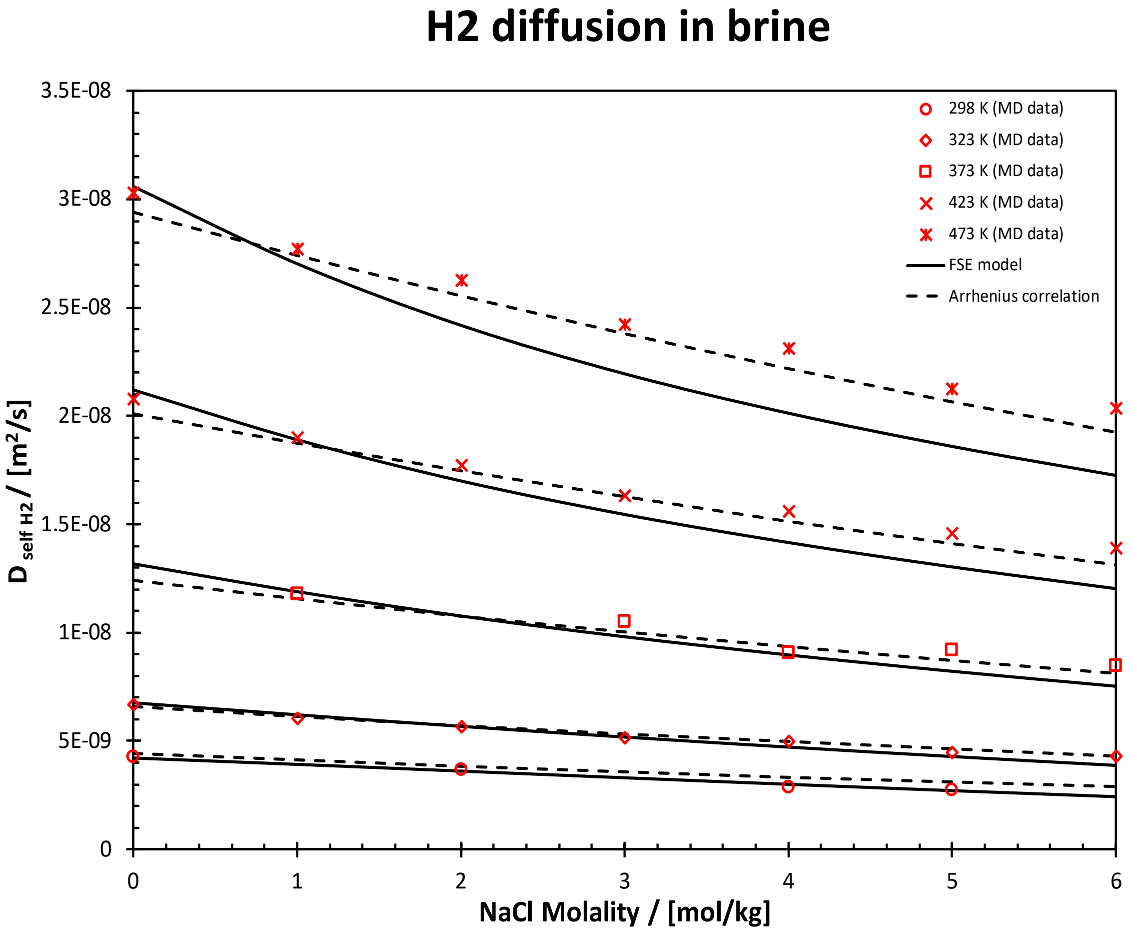
D ⇗ with T

D weakly ⇘ with P

D ⇘ with m

- ✓ **Results** weakly **depend** on the **water model !**
- ✓ **Data are consistent with experiments** (but about 25 % lower)

H2 DIFFUSION MODELING IN NACL BRINE



Fractional Stokes-Einstein

$$D^{1/s} = k_B T/(n_{SE}\pi\eta a)$$

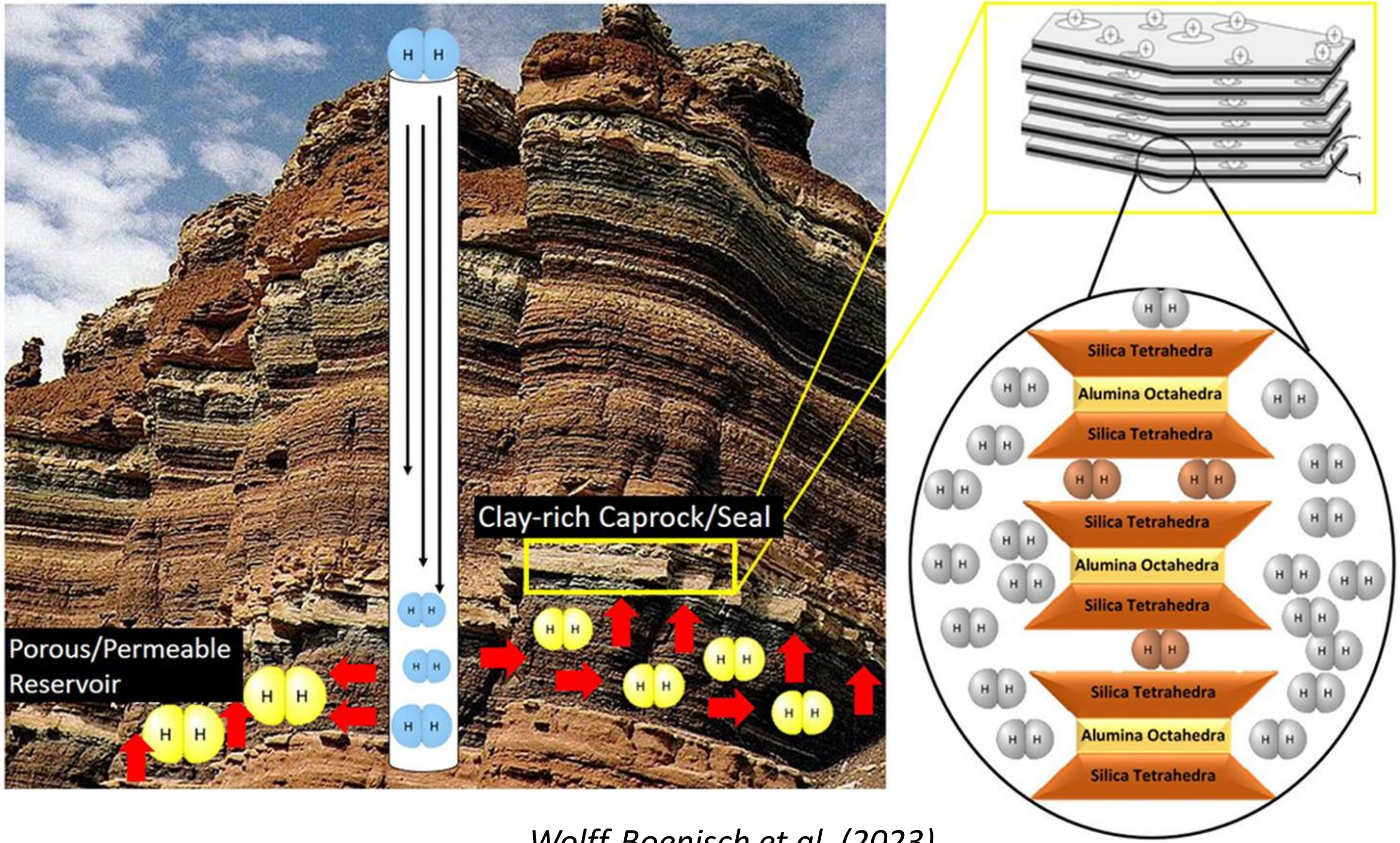
Arrhenius like correlation

$$\ln D = \ln D_o + \frac{E_D}{RT} + k_s m_s + k_P P$$

- ✓ **Arrhenius type and Fractional Stokes-Einstein** are **adequate**
- ✓ **Viscosity** of the **brine** is the **key quantity**

HYDROGEN DIFFUSION IN SATURATED CLAY

HYDROGEN BEHAVIOR IN THE PRESENCE OF CLAY



Wolff-Boenisch et al. (2023)

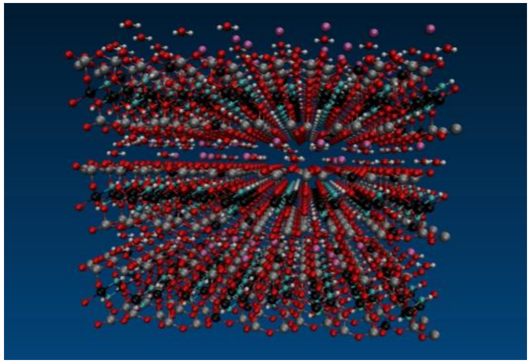
Oversolubility ? **Mobility ?**

Availability = solubility x mobility

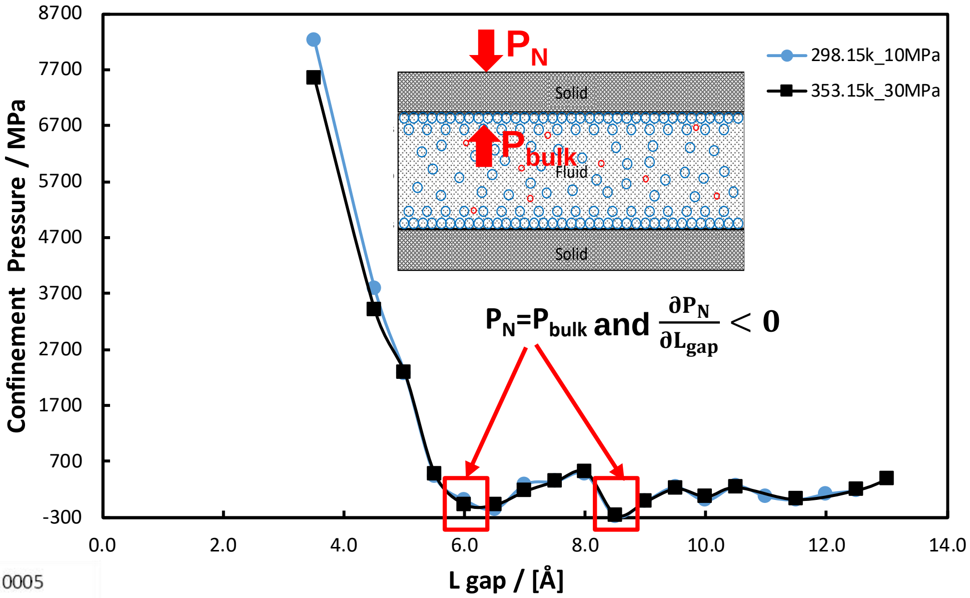
Benazzouz et al. (2022)

H2 DIFFUSION IN SATURATED ILLITE

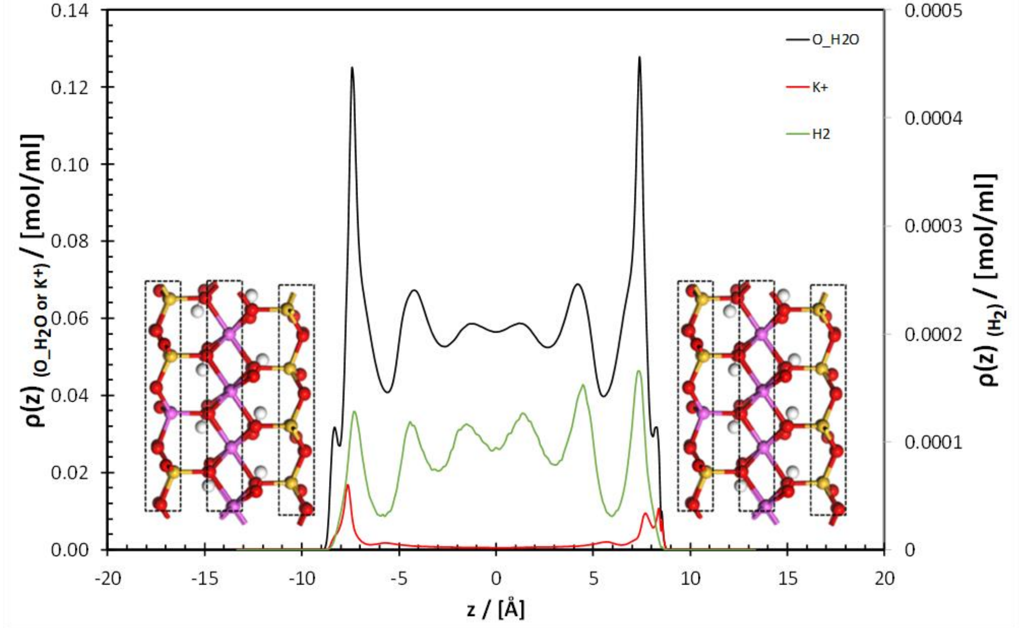
Simulated system snapshot



Confinement Pressure



Fluid distribution in the pore



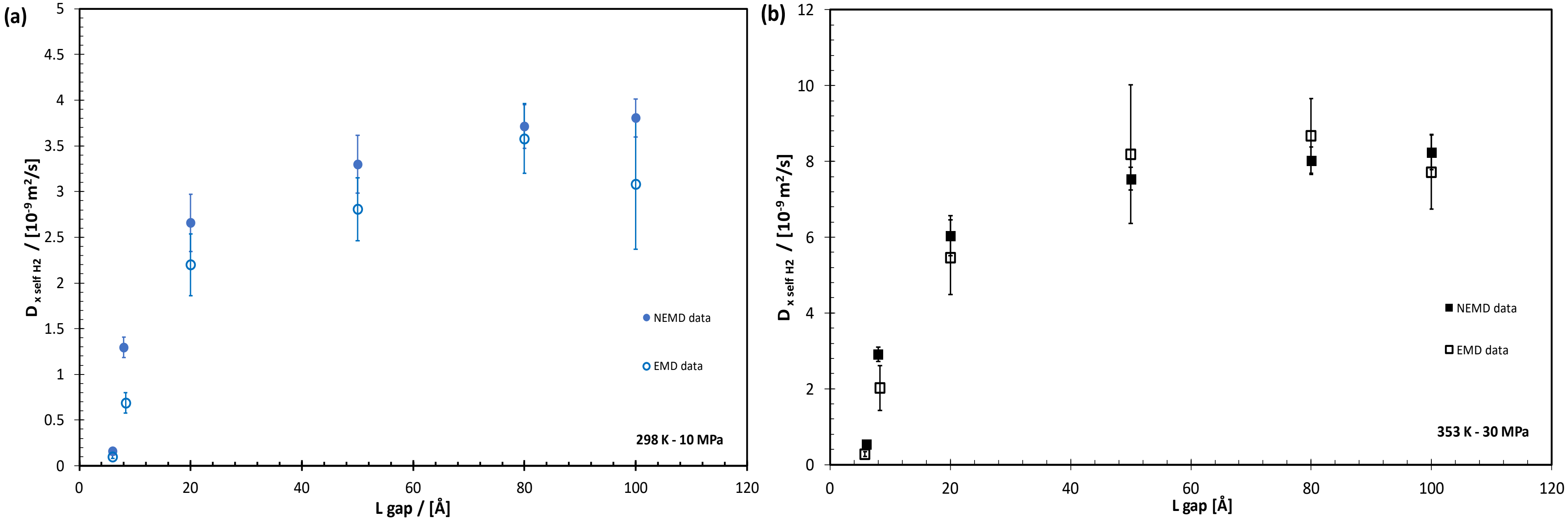
- ✓ **One & two layers water** exist
- ✓ **Water** is **adsorbed**
- ✓ **H2** is **not adsorbed !**

H2 uptake and not *adsorption*!

H2 DIFFUSION IN SATURATED ILLITE : EMD VS NEMD

T = 298.15 K and *P* = 10 MPa

T = 353.15 K and P = 30 MPa

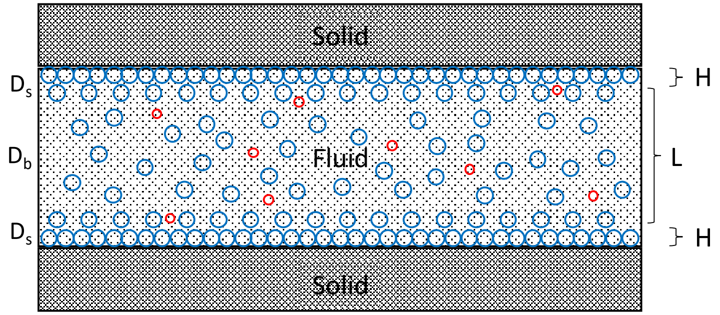


Kerkache et al., submitted

- ✓ **NEMD** provided **lower uncertainties** for high pore size
- ✓ **H2 diffusion ⬂ with confinement** (but less than one ordre of magnitude)

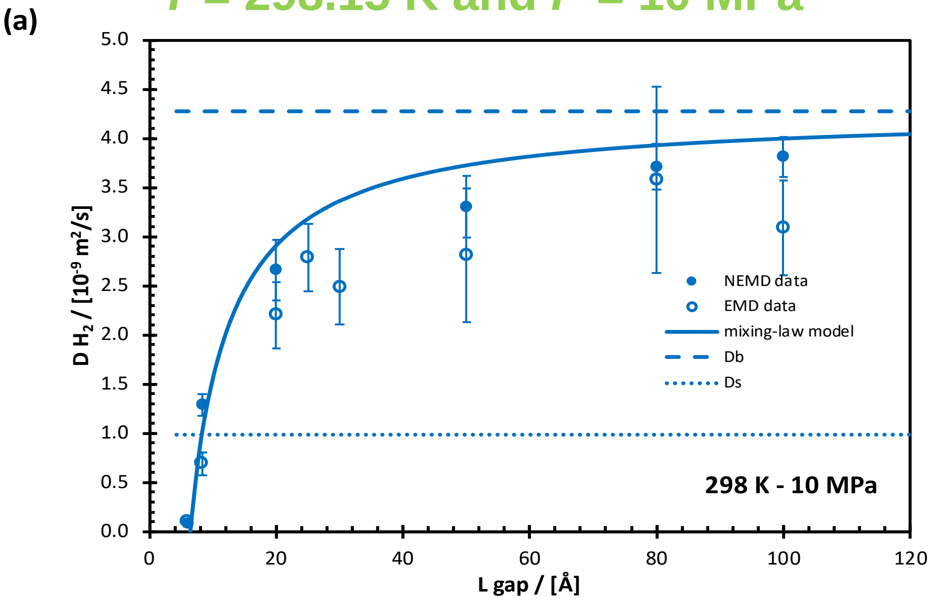
H2 DIFFUSION IN SATURATED ILLITE: MODELING

Two layers Model

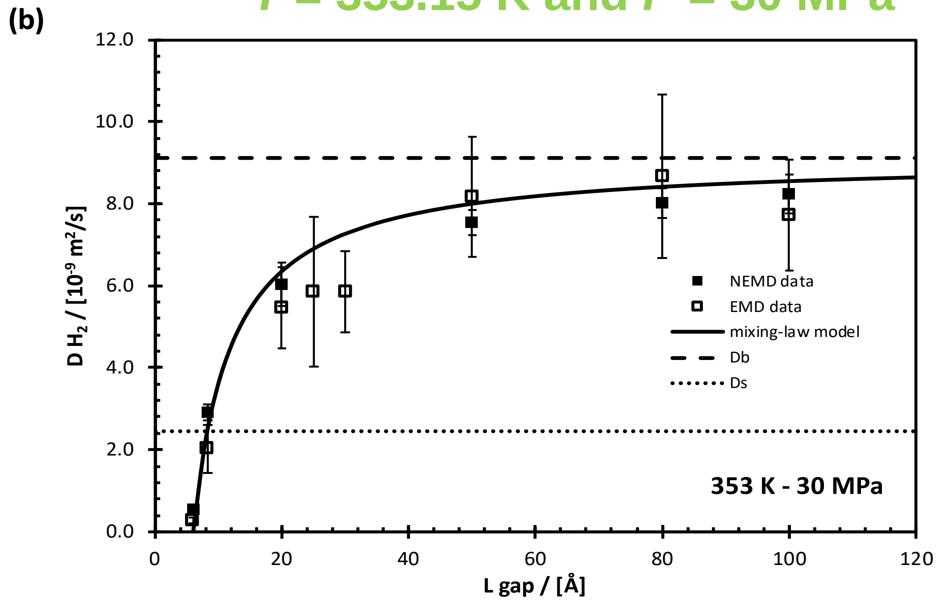


Arithmetic mean effective model

T = 298.15 K and *P* = 10 MPa



T = 353.15 K and *P* = 30 MPa



- ✓ Simple surface+bulk // diffusion model works !
- ✓ Surface diffusivity knowledge could be sufficient

CONCLUSIONS

TAKE HOME MESSAGES

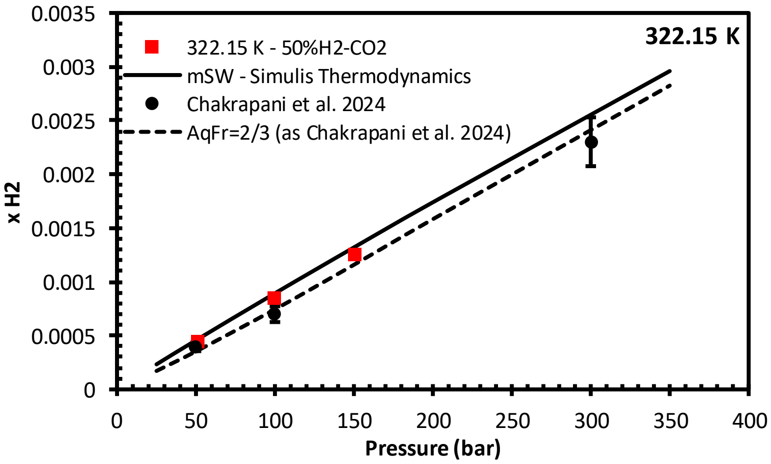
- ✓ **Experimental measurements**
  - ○ Difficult to achieve with H_2 but are crucial
  - ○ New data available for H_2 solubility and diffusion in brine

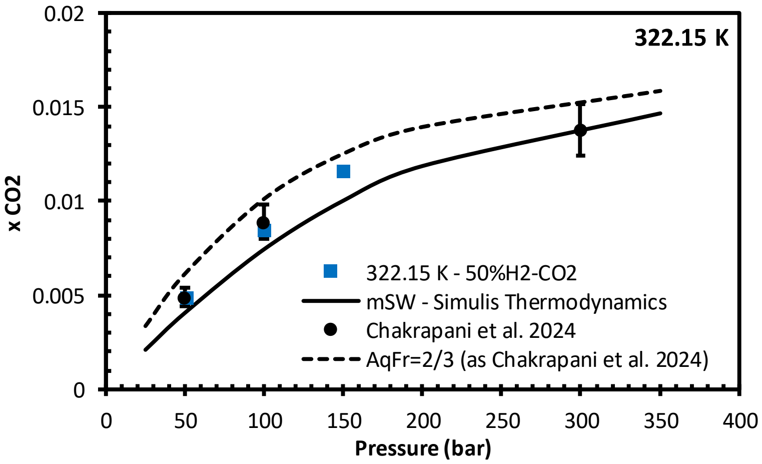
- ✓ **Molecular simulation capabilities**
  - ○ Able to provide quasi experimental results on H_2 + Brine
  - ○ Help in understanding microscopic behavior

- ✓ **Developing models**
  - ○ Classical approaches are applicable to deal with H_2+Brine
  - ○ Physicaly based models are more robust than correlations

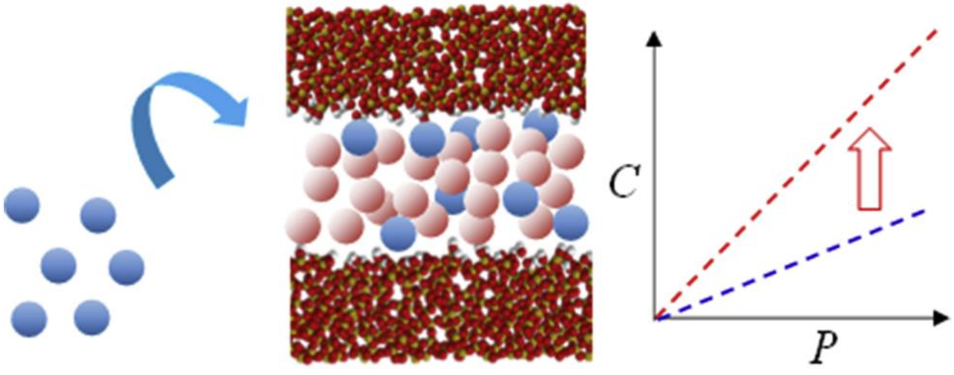
NEXT STEPS

Co-solubility/diffusion in H_2-CO_2/Water-Brine



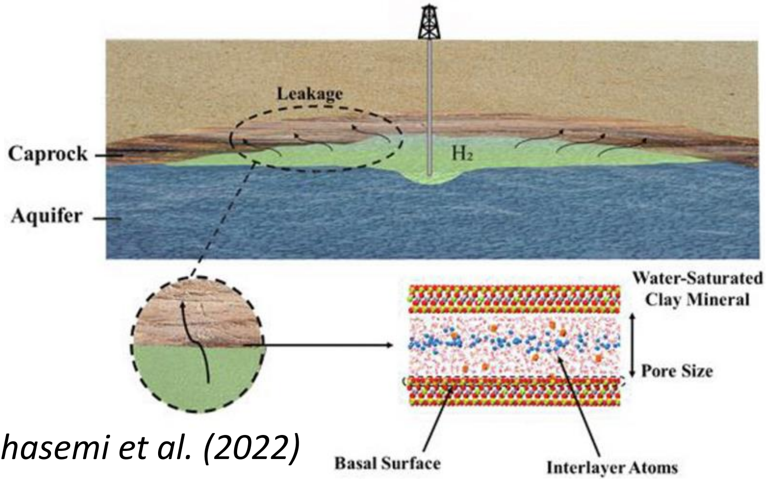


Hydrogen Oversolubility (not adsorption !)



Coasne & Farrusseng (2019)

H_2 Availability/migration in clay



Ghasemi et al. (2022)

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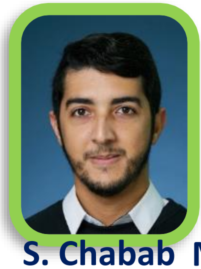
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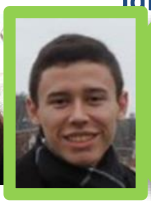
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THANK YOU FOR YOUR ATTENTION !

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