ÉTUDE DE LA DISSOLUTION DE L'HYDROGÈNE DANS LA SAUMURE DANS LE CADRE DU STOCKAGE EN NAPPE AQUIFÈRE

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Post-doc (bientôt)

Chaire junior HYDR
Lancée en avril 2021
Durée : 5 ans
RESEARCH PROJECT: JUNIOR CHAIR HYDR

Scope
✓ $\text{H}_2$ (+ NG and/or CO$_2$) mobility in Aquifers
✓ $\text{H}_2$ Storage, Natural $\text{H}_2$ exploration, and Geothermal energy

Framework (E2S)
✓ HYDR Junior Chair (S. Chabab)
✓ Exps + Mol Sim + EoS Models
✓ LFCR + LATEP + ProSim + IFPEN

Activities/Projects
- PhD (2021-2024, H. KERKACHE): Solubility + Diffusion in brine and clay. Mol Sim + exps
- PDRA (2022-2024, ProSim): Advanced Modeling
- Implementation in ProSim Tools
Multi-scale parameters relevant in Underground Hydrogen Storage

Underground hydrogen storage (UHS)

Influencing factors

Solid properties
- Absolute permeability ($k_a$);
- Effective porosity ($\phi_{\text{effective}}$);
- Effective stress ($\sigma_{\text{effective}}$).

Fluid properties
- Density ($\rho$);
- Viscosity ($\mu$);
- Fluid-fluid interfacial tension ($\gamma_{\text{FF}}$);
- Solubility;
- Diffusivity.

Solid-fluid interactions
- Wettability;
- Solid-fluid interfacial tension ($\gamma_{SF}$);
- Capillary pressure ($P_c$);
- Relative permeability ($k_r$);
- Mobility ratio ($M$);
- Saturation ($S$);
- Adsorption-desorption;
- Chemical reactions;
- Biology/bacteria.

Fluid properties

- Gas solubility
- Water content in gas phase
- Diffusion coefficient
- IFT (MS)

➔ Estimation of storage capacities and losses by dissolution
➔ Design / Simulation of surface facilities (e.g. gas dehydration after withdrawal)
➔ Gas reactivity study
➔ Estimate the amount of cushion gas
REVIEW OF AVAILABLE H₂ SOLUBILITY DATA: INCONSISTENCIES

- Only 2 experimental studies (P > P_{atm}) :
  - Chabab et al. 2020 (capillary sampling + GC at known T/P)
  - Torín-Ollarves & Trusler 2021 (bubble-point pressure at known T/x)
- 1 MS study: Lopez-Lazaro et al. 2019

- Large deviations (up to 30%) between the reported data

=> Interest to conduct more studies: Experimental and Molecular Simulation!
Characterization of $\text{H}_2$ (+ gas) dissolution in aquifers

Apparatus for measuring gas solubility in liquids: presentation and validation of the protocol
**Laboratory tests (LaTEP lab)**
Protocol development and validation

**Characterization of H₂ (+ gas) dissolution in aquifers**

Adaptation of an existing apparatus
- Old analytical technique: potentiometric titration
- **New analytical technique**: Volumetric & gravimetric

- Verification of pressure equipment
- Change of fluid: Change from a "Group 2 gas" fluid to a **"Group 1 gas"** fluid
CHARACTERIZATION OF $\text{H}_2$ (+ GAS) DISSOLUTION IN AQUIFERS

Sample collection in the Flash pycnometer

Flash pycnometer

Equilibrium Cell

Gasometer

+ GC (if gas mixture)
Sampling and analysis

$\mathbf{m}_0$, $\mathbf{m}_1$, $\mathbf{m}_2$

Sampling

Degassing
Validation of the apparatus on the CO$_2$+H$_2$O system

New data vs Literature data (for validation purpose)

**Method 1: Volumetric determination**

<table>
<thead>
<tr>
<th>Sample</th>
<th>P (MPa)</th>
<th>T (K)</th>
<th>GLR (Nm$^3$/m$^3$)</th>
<th>Sample size (g)</th>
<th>$m_{\text{Gas}}$ (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt1</td>
<td>4.57</td>
<td>321.55</td>
<td>15.81</td>
<td>62.85</td>
<td>1.96</td>
</tr>
<tr>
<td>Pt2</td>
<td>4.65</td>
<td>323.45</td>
<td>15.71</td>
<td>16.40</td>
<td>0.48</td>
</tr>
<tr>
<td>Pt3</td>
<td>4.63</td>
<td>323.45</td>
<td>15.65</td>
<td>26.82</td>
<td>0.81</td>
</tr>
<tr>
<td>Pt4</td>
<td>7.53</td>
<td>323.15</td>
<td>22.95</td>
<td>36.15</td>
<td>1.58</td>
</tr>
<tr>
<td>Pt5</td>
<td>10.30</td>
<td>324.75</td>
<td>26.13</td>
<td>10.47</td>
<td>0.48</td>
</tr>
</tbody>
</table>

**Method 2: Gravimetric determination**

Repeatability / reproducibility check
CHARACTERIZATION OF $\text{H}_2$ (+ GAS) DISSOLUTION IN AQUIFERS

Verification of the non-dependence on the sample size

$X\text{CO}_2$ vs. sample size

$P=\left[45.7 - 46.5\right]$ bar / $T=\left[48 - 50\right] ^\circ \text{C}$
Measuring the $\text{H}_2$ dissolution in water and brine
CHARACTERIZATION OF H$_2$ ( + GAS) DISSOLUTION IN AQUIFERS

Measurements of H$_2$ solubility in pure H$_2$O:

➔ 8 equilibrium points at 50°C (7 – 20 MPa)

- Results consistent with literature data
- Due to the low H$_2$ solubility, measurements are easier at high-pressure (better repeatability and less uncertainty)
Characterization of H₂ (+ gas) dissolution in aquifers

Measurements of H₂ solubility in 1m NaCl brine:
8 equilibrium points at 50°C (10 – 20 MPa)

- Closer to Torín-Ollarves & Trusler 2021 than Chabab et al. 2020 data
- Torín-Ollarves & Trusler 2021 and this work expect a lower salting-out than that reported by Chabab et al. 2020
Studying the $\text{H}_2$ solubility using Monte Carlo simulation
WHAT IS AND WHY MOLECULAR SIMULATION?

- High-performance computing (HPC)
- Force field
- Statistical method (Monte Carlo)
- Newton’s law of motion (Molecular Dynamics)

• 2 tools are used for the calculation of H₂ solubility by performing Monte Carlo simulations: **Towhee** and **Brick-CFCMC**

![MCCCS Towhee](image1)

![Brick-CFCMC](image2)

• Model choice:

**Pure H₂ model:** Alavi, Marx

**Pure H₂O model:** SPC/E, TIP4P/2005


• Use of different methods for the calculation of solubility
**Molecular Simulations: Force Fields**

**H₂**

<table>
<thead>
<tr>
<th>Model/atom</th>
<th>q⁺ (e)</th>
<th>q⁻ (e)</th>
<th>ε (K)</th>
<th>σ (Å⁺)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alavi 2005</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-H₂</td>
<td>0,4932</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>M-H₂</td>
<td>-</td>
<td>-0,9864</td>
<td>34,3</td>
<td>3,038</td>
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<tr>
<td>Marx 1992</td>
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<td>H-H₂</td>
<td>0,4680</td>
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<td>-</td>
<td>-</td>
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<tr>
<td>M-H₂</td>
<td>-</td>
<td>-0,9360</td>
<td>36,7</td>
<td>2,958</td>
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**H₂O**

<table>
<thead>
<tr>
<th>Model/atom</th>
<th>q⁺ (e)</th>
<th>q⁻ (e)</th>
<th>ε (K)</th>
<th>σ (Å⁺)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPC/E</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>O</td>
<td>-</td>
<td>-0,8476</td>
<td>78,175</td>
<td>3,166</td>
</tr>
<tr>
<td>H</td>
<td>0,4932</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TIP4P/2005</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>-</td>
<td>-</td>
<td>93,196</td>
<td>3,1589</td>
</tr>
<tr>
<td>H</td>
<td>0,5564</td>
<td>-</td>
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<td>-</td>
</tr>
<tr>
<td>Q</td>
<td>-</td>
<td>-1,1128</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**EVALUATION OF FORCE FIELDS : PURE HYDROGEN H₂**

- **At 160K**: Among the two models tested, the Alavi model captures well the compressibility factor ($\text{AAD}_{\text{Alavi}}=1.5\%$) at low temperature and so the quantum effects.

- **At 400K**: The model of Marx predict well the compressibility factor ($\text{AAD}_{\text{Marx}}=0.49\%$). However, Alavi is less accurate at high temperature ($\text{AAD}_{\text{Alavi}}=2.17\%$).

*Storage conditions in aquifers* $T=[293-373K]$, $P[50-500\text{bars}]$
**Evaluation of Force Fields: Pure Hydrogen $H_2$ at 323 K**

- **At 323K**: all the models predict well the compressibility factor, the AAD obtained are less than 1. ($\text{AAD}_{\text{Alavi}}=0.97\%$, $\text{AAD}_{\text{Marx}}=0.53\%$)
EVALUATION OF FORCE FIELDS: PURE WATER H₂O
THE DIFFERENT METHODS FOR THE CALCULATION OF SOLUBILITY

- **$H_i$:** The solubility of hydrogen in water/brine can be calculated using the **Henry constant**, which is related to the residual chemical potential of the solute $i$ at infinite dilution $\mu_i^\infty$:

  \[
  H_i = \rho k_B T \exp(\mu_i^\infty / k_B T)
  \]

  where $k_B$ is the Boltzmann constant, $T$ the temperature, $\rho$ the density of the solvent.

  $\mu_i^\infty$: from molecular simulation (MSMC: 1 boxe-NPT ensemble + widom insertion)

- **using Gibbs ensemble** (2 boxes - NPT ensemble)

- **Equality of chemical potentials:** NPT simulations => plot the chemical potential as a function of hydrogen composition => the intersection of the two curves (liquid and vapor) represents the solubility of hydrogen at the fixed conditions.

### Table: NPT simulations

<table>
<thead>
<tr>
<th>N simulations</th>
<th>$H_2$</th>
<th>$H_2O$</th>
<th>$H_2O$</th>
<th>$H_2$</th>
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<tbody>
<tr>
<td>1</td>
<td>600</td>
<td>1</td>
<td>730</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>600</td>
<td>2</td>
<td>730</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>600</td>
<td>...</td>
<td>730</td>
<td>...</td>
</tr>
<tr>
<td>4</td>
<td>600</td>
<td>...</td>
<td>730</td>
<td>...</td>
</tr>
</tbody>
</table>

### Graph: Chemical potential ($\mu_{\text{excess},i}$) vs. composition ($x_i$ or $y_i$)
At high temperature (T>353K), the SPC/E model does not capture well the water density => test a new force field for water: TIP4P/2005
HENRY COEFFICIENT- \( H = f(T) \)

Effect of density on the qualitative representation of \( H \) vs. \( T \)

By fixing the density (exp) or by using a suitable model for water density (TIP4P/2005), the results are qualitatively much improved (\( H \) vs. \( T \))

What can be done to quantitatively improve predictions?
- Using the **Marx** model for H$_2$ (also used by Lazaro et al. 2019, IFPEN) significantly **improves** the predictions.
SOLUBILITY ($x_{H_2}$) FROM HENRY COEFFICIENT

$$H_{H_2} = \frac{P \cdot \varphi_{H_2} \cdot y_{H_2}}{x_{H_2} \cdot Po_{yH_2}(P,T)} \quad with: \quad Po_{yH_2}(P,T) = \exp(\vartheta_{H_2}^{\infty} \frac{P - P^{sat}}{RT})$$

$$x_{H_2} = \frac{P \cdot \varphi_{H_2} \cdot y_{H_2}}{H_{H_2} \cdot Po_{yH_2}(P,T)}$$

$P$: Total pressure
$\varphi_{H_2}(T,P)$: fugacity coefficient of $H_2$ in the vapor phase
$y_{H_2}$: $H_2$ content in the vapor phase
$Po_{yH_2}(T,P)$: Poynting factor
$\vartheta_{H_2}^{\infty}$: partial molar volume of $H_2$ at infinite dilution

$\vartheta_{H_2}^{\infty} = f(T)$, It is assumed that $\vartheta_{H_2}^{\infty} \neq f(P)$

- From the literature (available only at $T=298.15^\circ \text{C}$ and $P=1 \text{ bar}$)
- From molecular simulation
SOLUBILITY ($x_{H2}$) FROM HENRY COEFFICIENT

$xH2$ calc [frac mol] vs $P$ [bar] for 323K.

Different data sets and models are plotted:
- Wiebe et al.
- Trusler et al.
- Chabab et al.
- this work: Alavi2005/SPCE - Brick
- this work: Alavi-TIP4P/2005 - Brick
- this work: Marx-TIP4P/2005 - Brick
- Rahbari et al.: Marx/TIP4P/2005 - Brick
Thermodynamics modeling of the $\text{H}_2 + \text{H}_2\text{O} + \text{NaCl}$ system
I) Symmetric approach (phi-phi)

\[ x_i \Phi_i^{Liq} = y_i \Phi_i^{vap} \]

1) Soreide and Whitson (SW) EoS
   - Peng-Robinson EoS with different BIPs (T and salinity dependent) for liquid and gas phases and a specific alpha-function for brine.
   - Recent parameters from Chabab et al. 2021

II) Asymmetric approach (gamma-phi)

3) Using Henry's constant

\[ x_i^{aq} y_i^{aq} H_i^g (T, P_{sat}) \exp \left( v_i^\infty \frac{P - P_{sat}}{RT} \right) = y_i^g \varphi_i^g P \]

4) Duan-type model

\[ \mu_i^{L(0)} + RT \ln(y_i) + RT \ln(x_i) = \mu_i^{v(0)} + RT \ln(y_i P) + RT \ln(\varphi_i) \]
THERMODYNAMICS MODELING OF THE $\text{H}_2 + \text{H}_2\text{O} + \text{NaCl}$ SYSTEM

$T = 323.15 \text{ K}$

**$\text{H}_2 + \text{H}_2\text{O}$**

![Graph](image1)

**$\text{H}_2 + \text{H}_2\text{O} + 1\text{m NaCl}$**

![Graph](image2)
1) Salting-out effect of CH$_4$, N$_2$, O$_2$, and H$_2$ in 1m NaCl brine

<table>
<thead>
<tr>
<th></th>
<th>CH$_4$</th>
<th>O$_2$</th>
<th>N$_2$</th>
<th>H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$100^\ast(1-x_{\text{in brine}}/x_{\text{in water}})$</td>
<td>25.35</td>
<td>25.38</td>
<td>25.24</td>
<td>17.18 (This work)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>12.25 (Torín &amp; Trusler 2021)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>24.28 (Chabab et al. 2020)</td>
</tr>
</tbody>
</table>

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$_2$ Ratio Gas Solubility Mystery.)
CONCLUSIONS

Summary

• Importance of thermophysical properties for UHS
• Impact of density and chemical potential on solubility prediction (MC simulation)
• Different approaches for the calculation of solubility
• Predictive capacity of MS
• Salting-out effect
• Gas solubility dependencies

Upcoming work

• Mixed-gas co-solubility (cushion gas, underground bio-methanation, etc.)
• H₂ diffusivity in brine
• Interfacial tension of H₂/mixed gas with brine (short/medium term)
• Impact of clay (long term perspective)
Thank you for your attention!

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Olivier BAUDOUIN (ProSim)
Colleagues from IFPEN
Christophe COQUELET (Mines)
Additional slides
Overview of the different types of energy storage

Principal types of underground gas storage


Ref: J.I.T. Force (2016), Underground natural gas storage: Integrity and safe operations
Effect of degassing in geothermal processes:

- Reducing the process efficiency
- pH change: salt (e.g., calcite-CaCO3) scaling
- Causing undesired GHG emissions

- Gas breakout depth
- Working pressure in surface facilities
APPLICATION TO DEGASSING IN GEOTHERMAL PROCESSES

✓ Duhring lines of equal Gas solubility in different brines
✓ Mutual Solubilities of Gas-Brine (Single or Mixed Salts)
✓ Mixed-gas cosolubility

Prediction of:

✓ Bubble-Point Pressure and

✓ GHG Emission Rate ($g$-eqCO2/kWh) in the Upper Rhine Graben Geothermal Sites

Selected models:

❖ Phase equilibria: EoS (Søreide and Whitson) with new parameters

❖ GLR conversion: GERG-2008 for gas, Al Ghafri’s correlation for brine