Reactive transport modelling for underground gas storage

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Acknowledgment

The Project is co-founded by European Union

Outline

1. Reactive transport
2. Phase equilibria
3. Gas storage: oxygen reactivity
4. Extension to other gases

1

Reactive transport

Reactive transport code HYTEC since 1996

HYTEC

Flow

(Un)saturated, multiphase
Non-isothermal
Double porosity
Anisotropy

Thermodynamics

Phase equilibria, EOS
Non-ideal gas, solution
Multicomponent mixtures
Thermodynamic properties

Transport

Aqueous and gaseous
Advection, diffusion, dispersion
Particle transport

Biogeochemistry

Acid/base, redox
Precipitation, dissolution
Microbiological reactions
Isotopic fractionation

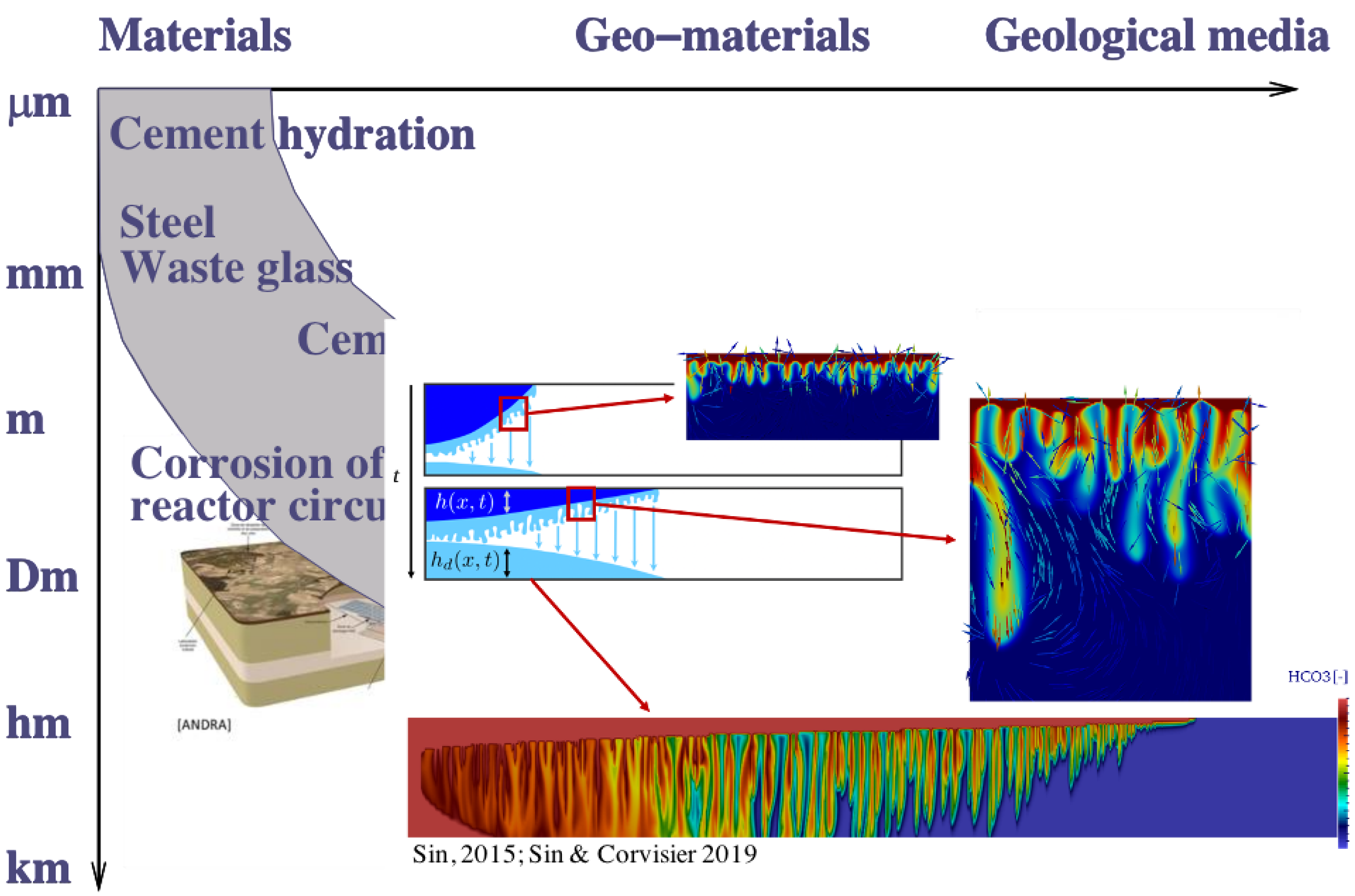
Mechanics

- **HYTEC**=**T**hermo+**H**ydro+**C**hemistry
- **CHESS** - geochemical core of HYTEC
- (Un)structured mesh
- History matching
- Coupling with mechanics
- Water balance
- Variable porosity
- Chemical and mechanical clogging

References

- van der Lee et al., Comp & Geos, 2003
- Sin, Lagneau and Corvisier, Adv. in Water Res, 2017
- Seigneur et al., Adv. in Water Res, 2018

Reactive transport code HYTEC since 1996



2

Phase equilibria

Phase equilibria

Assymetric approach

$$f_i^g = P y_i \varphi_i = K_i^H \gamma_i x_i = f_i^l$$

- φ is the fugacity coefficient calculated by EOS models: e.g. cubic EOS – Peng-Robinson (1978)

$$P = \frac{RT}{v - b^{\mathrm{PR}}} - \frac{a^{\mathrm{PR}}(T)}{v\left(v + b^{\mathrm{PR}}\right) + b^{\mathrm{PR}}\left(v - b^{\mathrm{PR}}\right)}$$

- K^H is the corrected Henry's constant

$$K_i^H(T,P) = K_g^{H,0}\left(T, P^{sat}\right) \exp\left[\frac{\left(P - P^{sat}\right) V_i^{\infty}}{RT}\right]$$

- γ_i is the activity coefficient (B-dot, SIT)

$$\ln \gamma_i = -\frac{A Z_i^2 \sqrt{I}}{1 + 1.5\sqrt{I}} + \sum_j [C_j]\epsilon_{ij}$$

Advantages

- Activity models adapted for aqueous geochemistry.
- K^H, BIP and EOS parameters adapted to non-ideal gases regarding P and T.
- Analytical solution for the PR-type EOS models.
- Group contribution structure, easy application for mixtures.

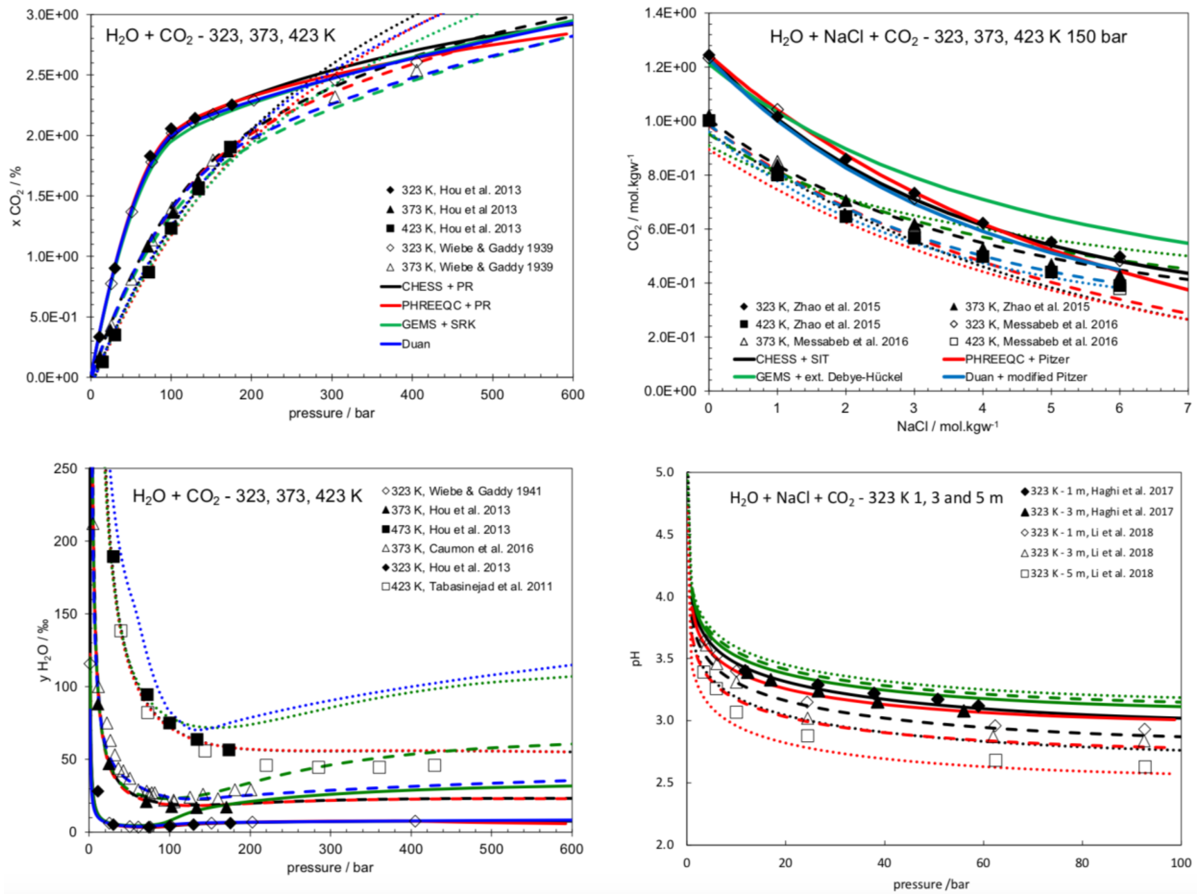
Required data

- φ: critical temperatures and pressures T_c, P_c, Z_c, Ω, mixing rule, binary interaction parameters
- K^H: Henry's constants at saturated vapor pressure, molar volumes for pressure correction
- γ_i: Debye-Hückel and B-dot general parameters, binary interaction parameters for solutes (SIT)
- Experimental lab of CTP&Geosciences, Mines Paris - PSL
- ANR GAZ ANNEXES, SIGARRR, FLUIDSTORY

Phase equilibria

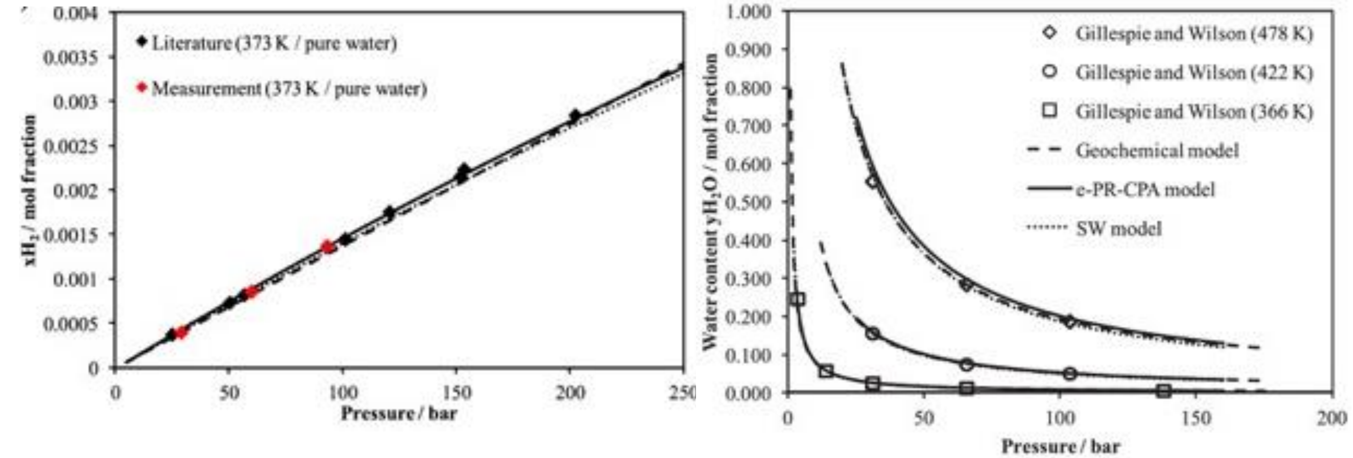
hystories
Hydrogen Storage in European Subsurface

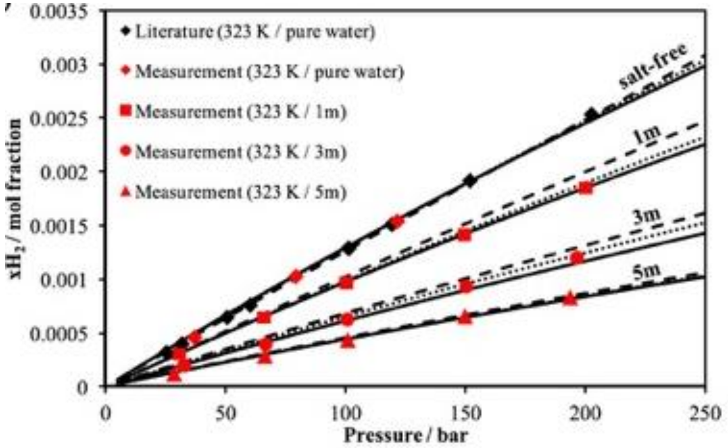
Solubility/reactivity of CO_2 in water and NaCl-brine



FluidSTORY project, Chabab et al., 2019, Sin and Corvisier 2019

Solubility of H2 in water and NaCl-brine





Database: CO_2, O_2, N_2, H_2, CH_4, H_2S, Ar, SF_6, C_2H_6, C_3H_8, C_4H_{10}, CO, He, Kr, Ne, NO, N_2O, Rn, SO_2, Xe

Rostock'H project, Carnot MINES, Chabab et al., 2020

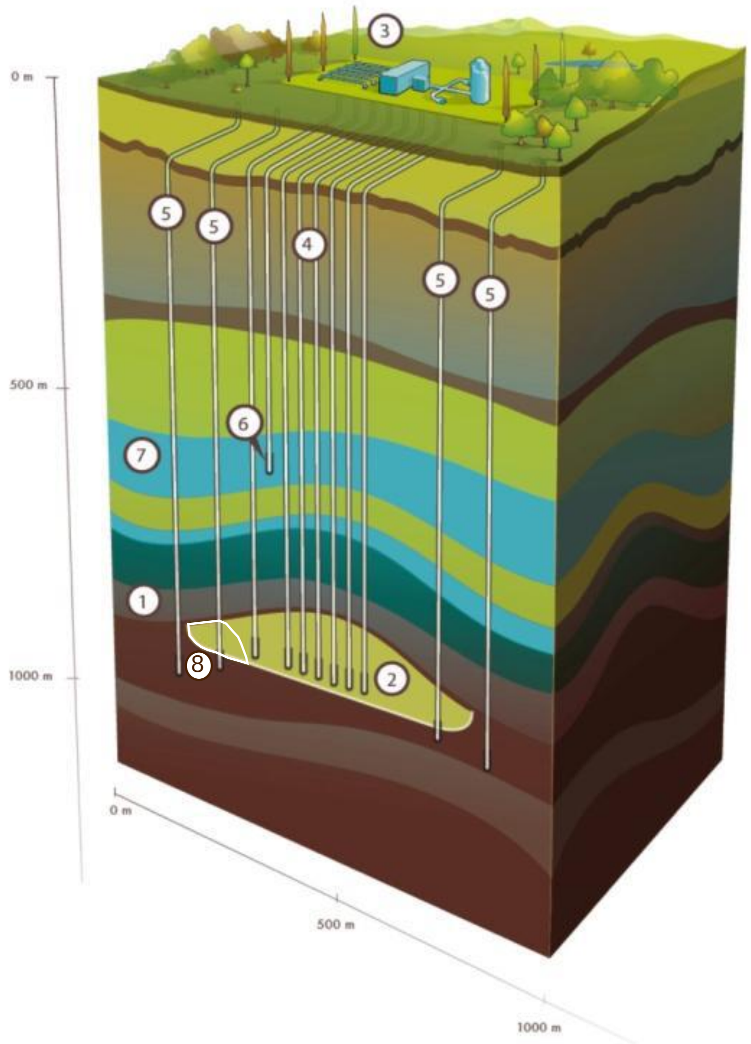
3

Gas storage: oxygen reactivity

Air injection into a sandstone reservoir (the Paris Basin)

hystories
Hydrogen Storage in European Subsurface

1) Caprock
2) Reservoir
3) Surface facilities
4) Injection and withdrawal wells
5) Monitoring wells
6) Monitoring wells of the upper aquifer
7) Upper aquifer
8) Cushion gas with O_2-depleted air



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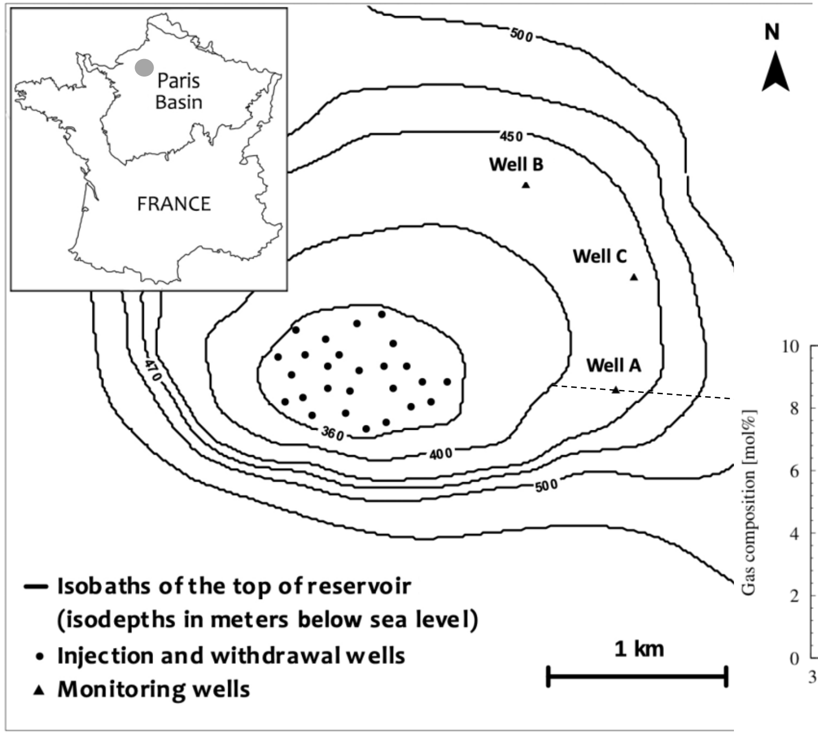
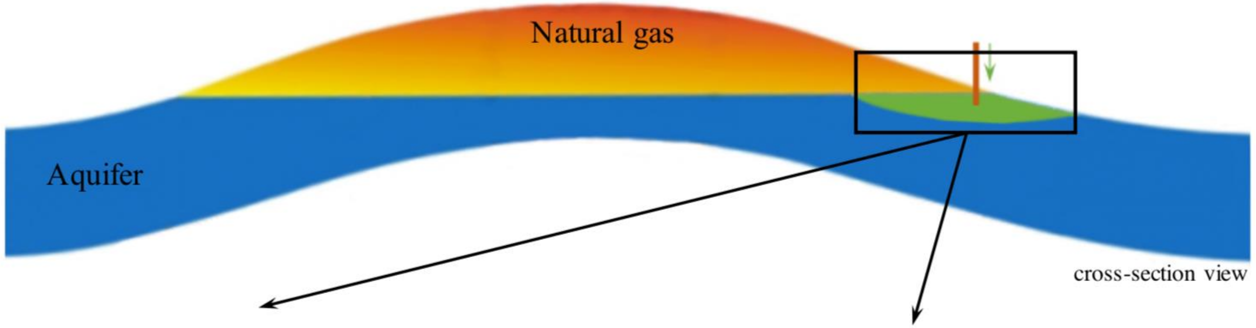
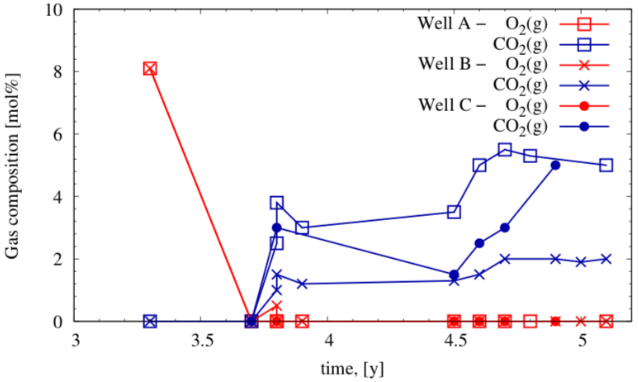
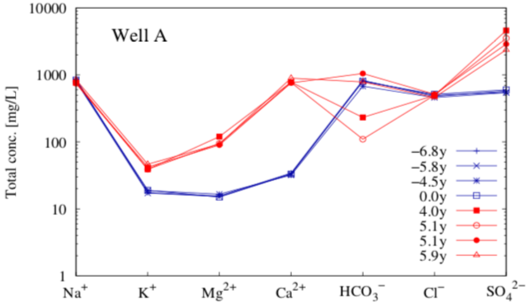
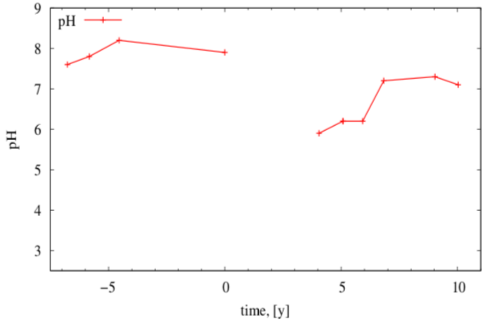
Air injection into a sandstone reservoir (the Paris Basin)

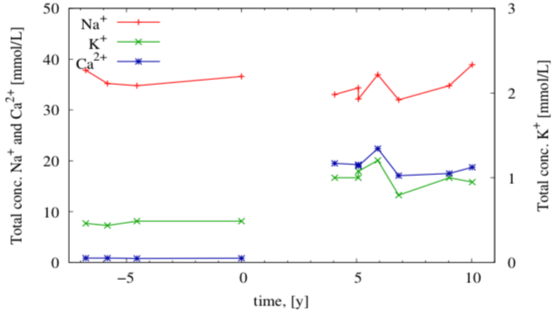


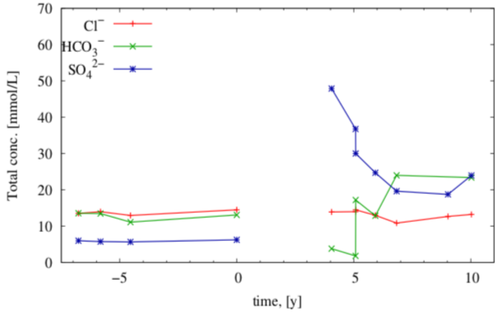






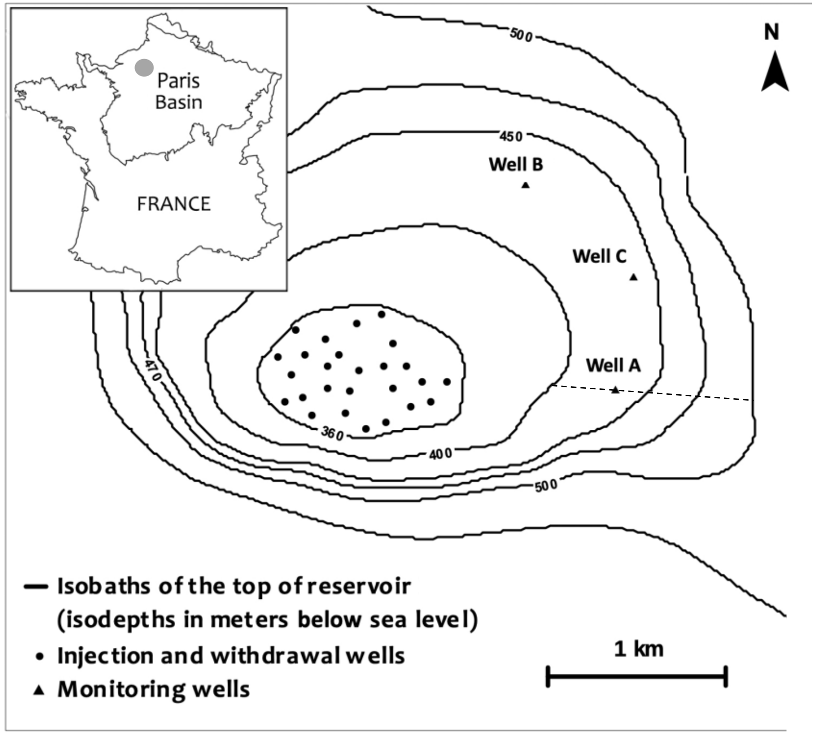


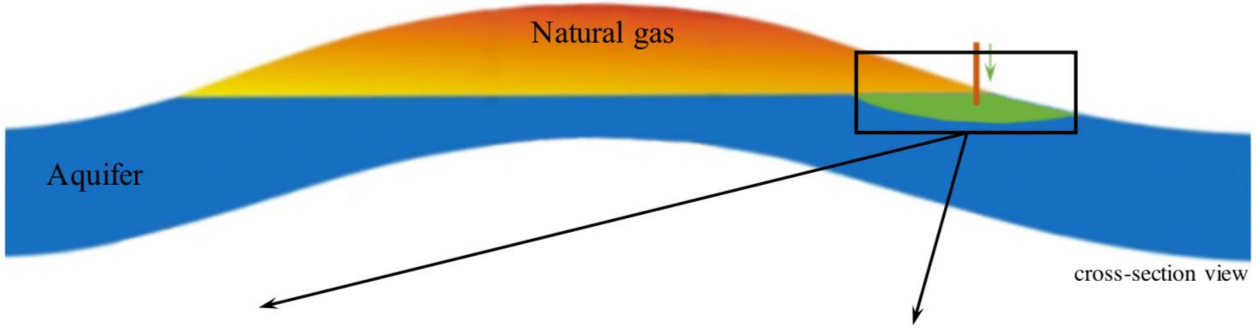


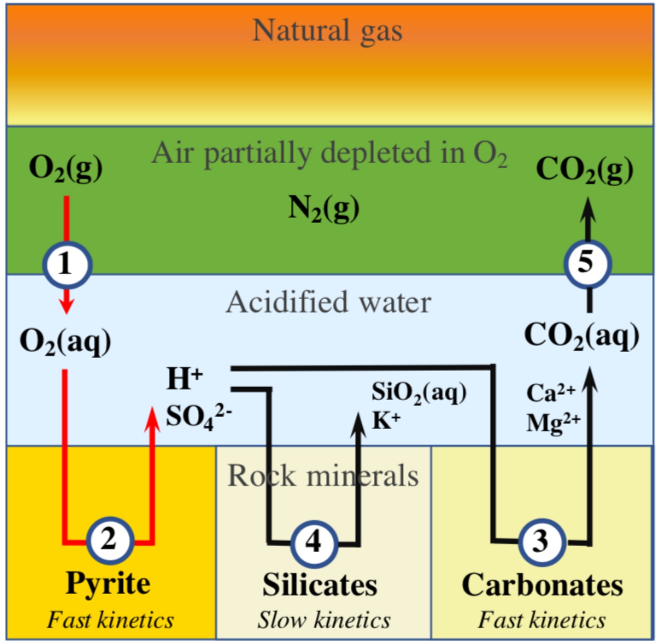


▶ What are the key mechanisms? What impact on the aquifer?

Gas-water-rock interactions







- Cushion gas: N_2, Ar, O_2
- Phase equilibrium of gases + $H_2O(g)$

$$O_2(aq) \rightleftharpoons O_2(g)$$

- Pyrite oxydation

$$\text{Pyrite} + 3.75O_2(aq) + 2.5H_2O \longrightarrow$$
$$\text{Goethite} + 2SO_4^{2-} + 4H^+$$

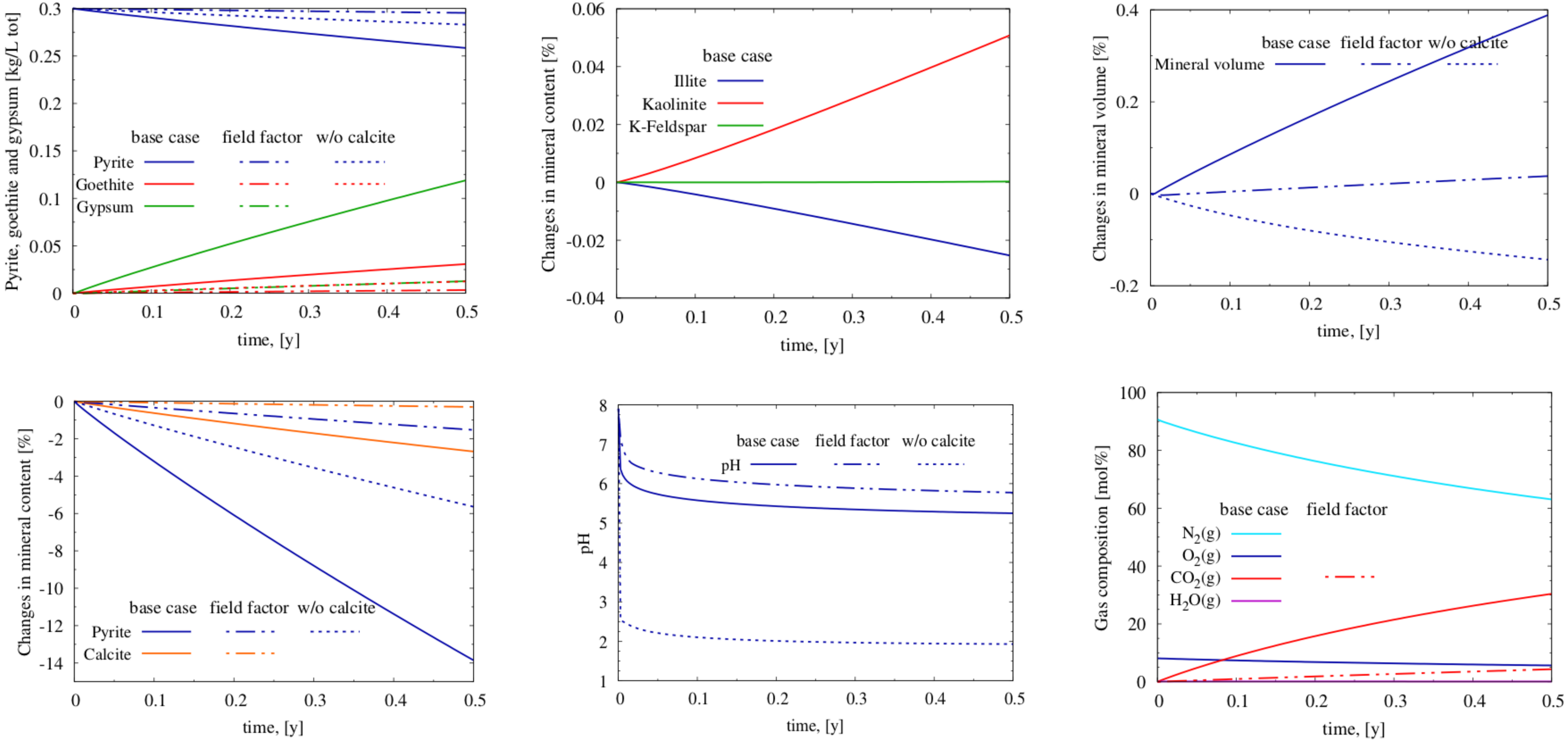
- Dissolution of calcite
  $\text{Calcite} + 2\,H^+ \longrightarrow Ca^{2+} + CO_2(aq) + H_2O$
- Exsolution of CO_2

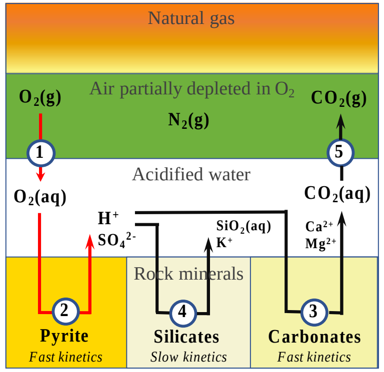
$$CO_2(aq) \rightleftharpoons CO_2(g)$$

- What are the key mechanisms? What impact on the aquifer?

Gas-water-rock interactions: batch modelling

hystories
Hydrogen Storage in European Subsurface





+ Available data (borehole water sampling and gas composition before and after injection) are used to establish the model.
+ Representation of major mechanisms vs site data.
- Closed system → production of CO_2 is overestimated.
➢ Reactive transport model is needed.

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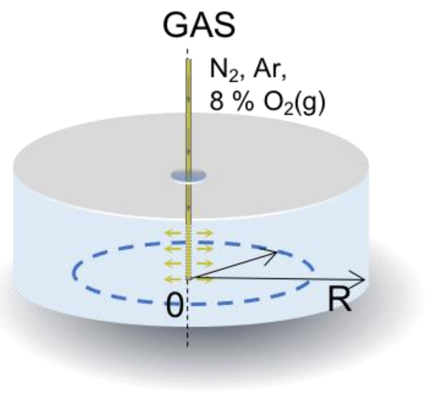
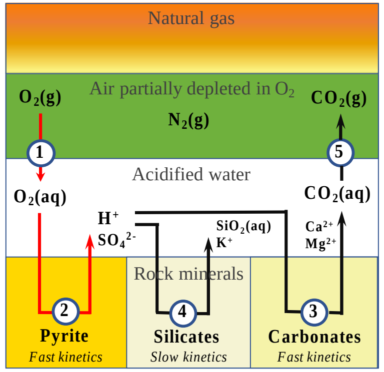
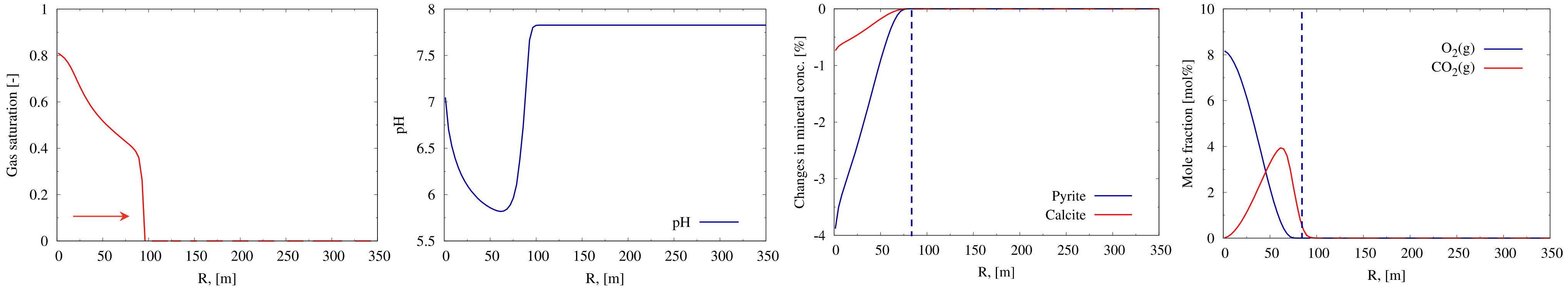
Radial 1D reactive transport model

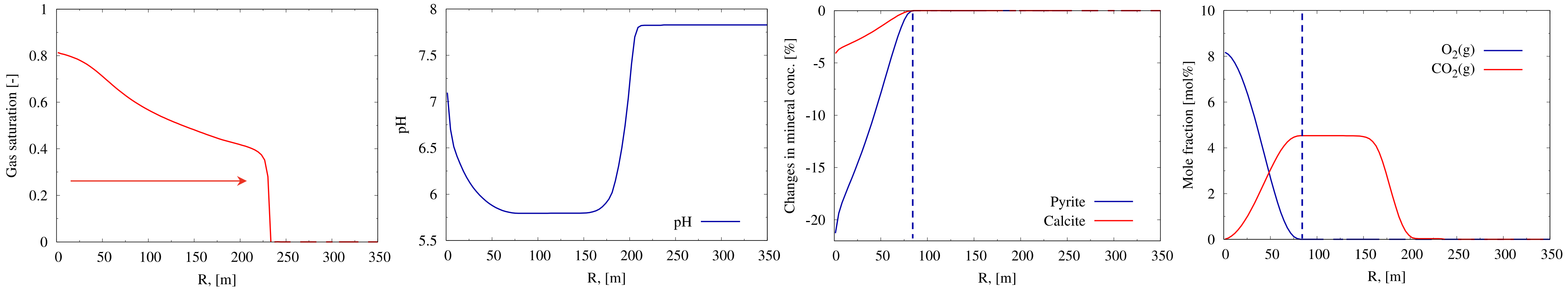




30 days

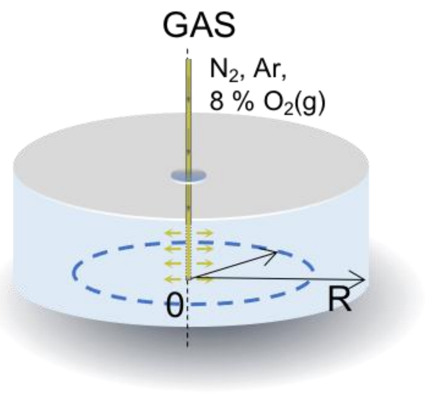


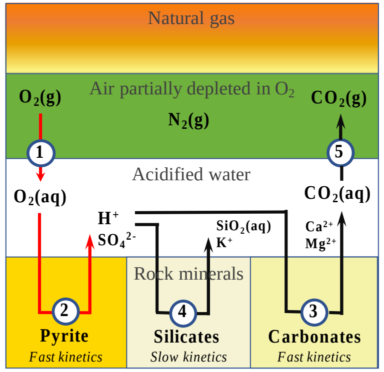
0.5 yr



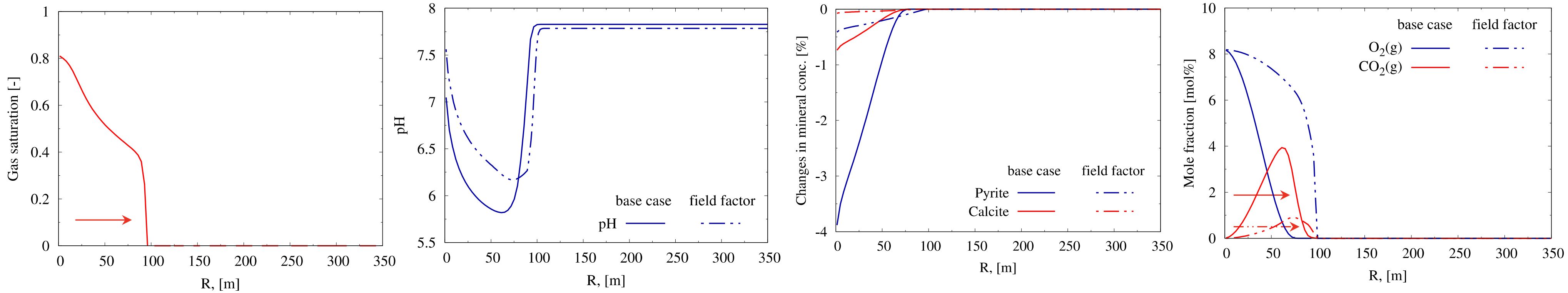
- Dissolution of pyrite/calcite → goethite/gypsum
- ! 22% of pyrite is dissolved. Rapid O_2 consumption (same profiles at 30 d and 0.5 yr)
- ! CO_2 accumulation grows with time, > 4 mol%
- ➤ A slower kinetics is needed

Radial 1D reactive transport model

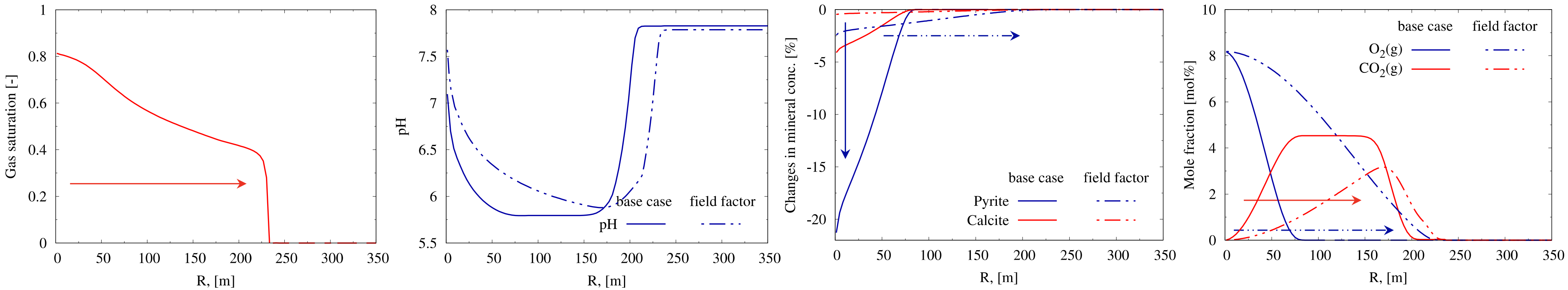




30 days



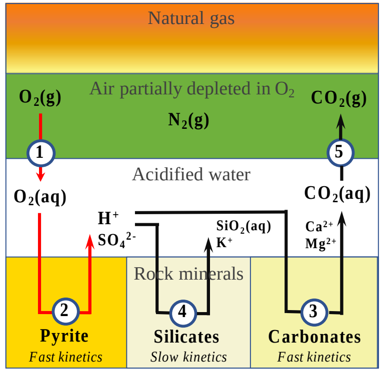
0.5 yr

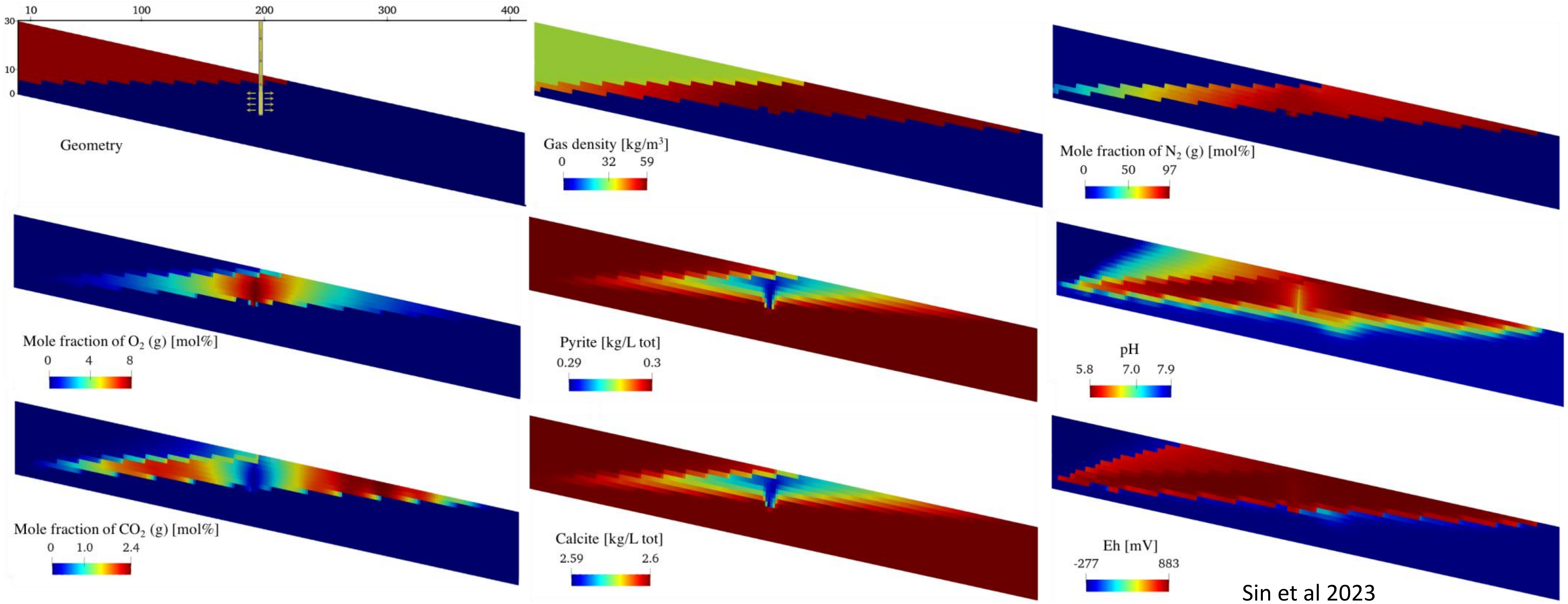


- Slower kinetics → ~2% of pyrite is dissolved.
- Slower O_2 consumption → O_2 can be transported further → pyrite oxydation not only at near-wellbore zone.
- Damköhler number is analysed, confirms the results.
- CO_2 accumulation still grows with time, ~ 3 mol%

➢ Radial 2D reactive transport model is needed…

Reactive transport model at reservoir scale





Sin et al 2023

- \+ Pyrite kinetics is a key factor: Damköhler number derived for O2 reactivity and pyrite kinetics explains gas changes.
- \+ The multiphase reactive transport model was built based on the field data. From batch to reservoir scales.
- ! Importance of reactive transport -> geometry/scale changing is game changing
- \+ This workflow can be applied for gas storage facilities (compressed air, biomethane, H_2)

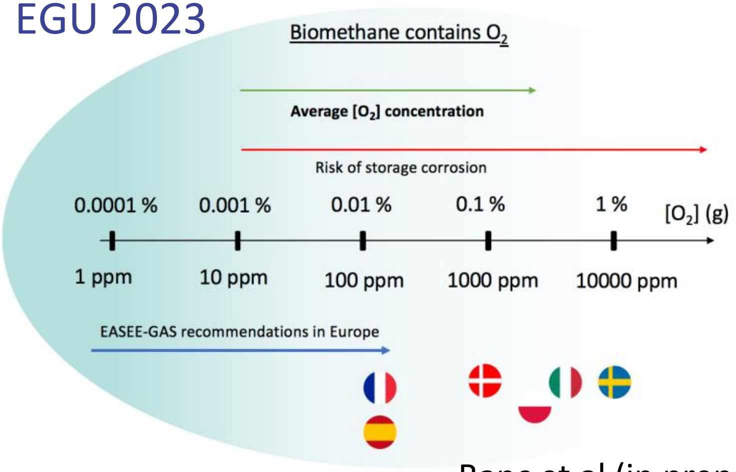
4

Extension to other gases

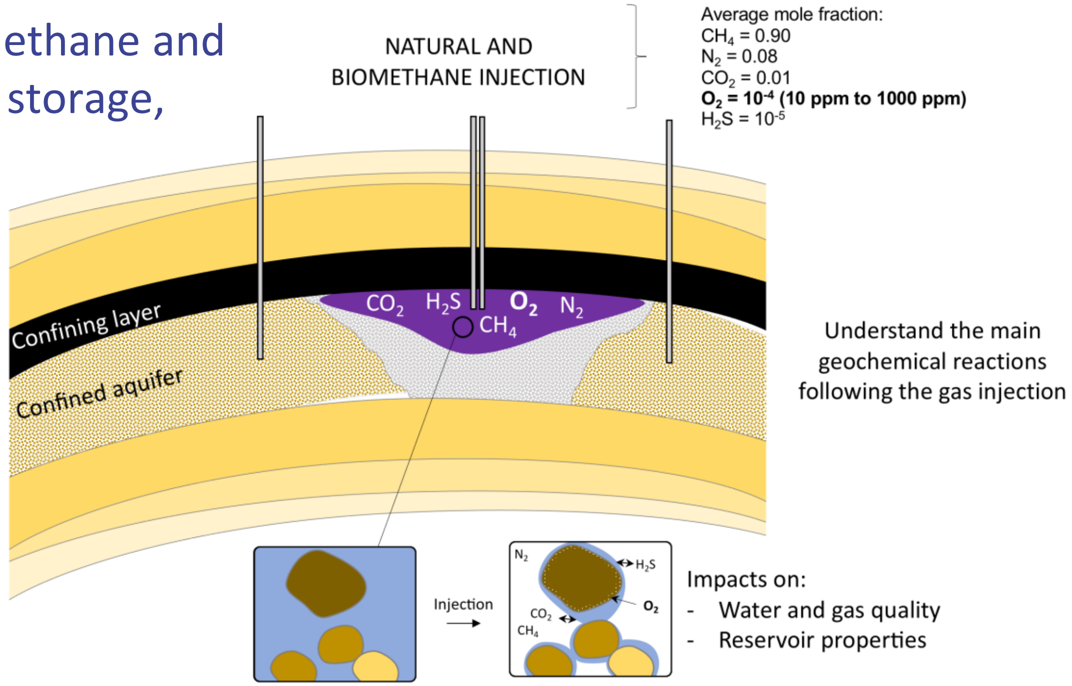
Extension to other gases

- **Biomethane and natural gas**

Evaluation of the geochemical impact of biomethane and natural gas mix injection in sandstone aquifer storage, EGU 2023



Banc et al (in preparation)



- **Hydrogen**
  - Additional complexity: microbial activity, parametrization of models.
  - Modelling experiments (Haddad et al 2022 etc) with Monod like laws
  - Upscaling, integrating to the storage model

HYTEC and consortium PGT

PGT Pôle Géochimie Transport

Reactive Transport Group

Since 2000, **PGT**

- shared funding
- shared scientific research
- shared expertise

PGT V 2020 - 2023

Thank you !