# Challenges of simulating multiphase flows in reactive porous media

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# Overview of the presentation

# HYTEC : a reactive transport code

- HYTEC : reactive transport code (Mines ParisTech for 15+ years )
- Based on two modules :
  - A hydrodynamic module (**R2D2**) : computes the flow (stationary, saturated, ...) and solute transport (diffusive, advective)
  - A geochemistry module (**CHESS**) : computes the chemical reactions : Speciation, redox, sorption, solid, kinetic reactions, ...
- Has been validated on numerous benchmarks on different applications
  - RW management, U in-situ recovery, cement degradation, ...
- User-oriented software which allows a user to model several flow and transport conditions with potentially high heterogeneity
- Historic Numerical algorithm : On one time-step
  1. Solving flow (saturated / unsaturated / transient / stationary)
  2. Reactive - Transport : sequential iterative approach
  3. Update properties (porosities, transport coefficients ...)

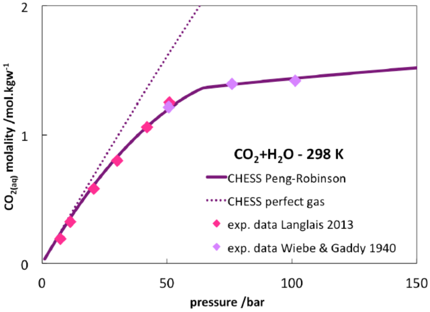
# Motivation and complications of two-phase flows

- Recent years : need to consider the gas phase for different applications :
  - Gas reservoirs, concrete degradation, ...
- Need to adapt the algorithm to take into account a gas phase
- Developments in the reactive transport community led to the description of multiphase flows
- PhD of Irina Sin : developed a fully coupled compressible two-phase flow inside Hytec.
  - Fast gaseous diffusion ; high impact of chemistry on flow ; need for an equation of state

# Overview of the presentation

# Gas-related Challenges

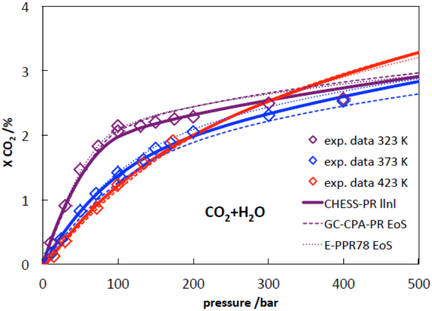
- In many applications, gases do not behave as ideal gases ...
- Simple mixing law for multicomponent gas phase (molar fraction $y_i$)

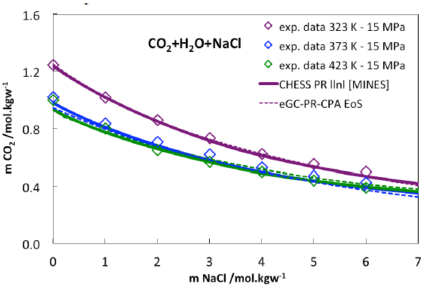



- Need of EOS to represent these
- Peng-Robinson EOS was implemented in CHESS/HYTEC :
  - Cubic equation with analytical solution : well suited to RTM !

# Peng-Robinson EOS

CHESS reproduced various experimental results with PR EOS




J. CORVISIER et al [2016]

- For Hytec, need to compute the gas-density :
  - EOS links pressure $p$ and molar volume $v$ : $p = f_{EOS}(v, T, y_i)$
  - Density is composition-dependent : $\rho_g = \frac{\sum y_i M_i}{v}$

# Overview of the presentation

# Mathematical framework - Flow

2-phase flow equations : Primary variables : $S_g$, $p_l$ ;

- $2^{nd}$ variables : $S_l = 1 - S_g$, $p_g = p_l + p_c(S_g)$,

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Continuity equation for each phase $\alpha$ :

$$\frac{\partial \omega S_\alpha \rho_\alpha}{\partial t} - \vec{\nabla} \rho_\alpha \vec{u_\alpha} = R_\alpha \tag{1}$$

$$\vec{u_\alpha} = -\frac{k_{r_\alpha}}{\mu_\alpha} K(\vec{\nabla} p_\alpha - \rho_\alpha \vec{g}) \tag{2}$$

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$$\frac{\partial \omega (1 - S_g)\rho_l}{\partial t} - \overrightarrow{\nabla} \rho_l \frac{k_{rl}(S_g)}{\mu_l} K(\overrightarrow{\nabla} p_l - \rho_l \overrightarrow{g}) = R_l \qquad (3)$$

$$\frac{\partial \omega S_g \rho_g}{\partial t} - \overrightarrow{\nabla} \rho_g \frac{k_{rg}(S_g)}{\mu_g} K(\overrightarrow{\nabla} (p_l + p_c(S_g)) - \rho_g \overrightarrow{g}) = R_g \qquad (4)$$

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$$\frac{\partial \omega S_g \rho_g}{\partial t} - \vec{\nabla} \rho_g \frac{k_{rg}(S_g)}{\mu_g} K(\vec{\nabla}(p_l + p_c(S_g)) - \rho_g \vec{g}) = R_g \quad (6)$$

- Capillary pressure $p_c$ and relative permeabilities $k_{rl}$, $k_{rg}$ (empirical)
- Gas-density : $\rho_g = f_{EOS}(T, p, y_i)$ → **coupling with gas transport !**
- Low-variable parameters : $\rho_l$, $\mu_l$, $\mu_g$
- Reactive-transport dependent : $\omega$, $R_l$, $R_g$, $K$

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$$\frac{\partial \omega S_g \rho_g}{\partial t} - \vec{\nabla} \rho_g \frac{k_{rg}(S_g)}{\mu_g} K(\vec{\nabla}(p_l + p_c(S_g)) - \rho_g \vec{g}) = R_g \quad (8)$$

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$$\frac{\partial \omega (1 - S_g)\rho_l}{\partial t} - \vec{\nabla} \rho_l \frac{k_{rl}(S_g)}{\mu_l} K (\vec{\nabla} p_l - \rho_l \vec{g}) = R_l \quad (9)$$

$$\frac{\partial \omega S_g \rho_g}{\partial t} - \vec{\nabla} \rho_g \frac{k_{rg}(S_g)}{\mu_g} K (\vec{\nabla} (p_l + p_c(S_g)) - \rho_g \vec{g}) = R_g \quad (10)$$

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$$\frac{\partial \omega S_g \rho_g}{\partial t} - \vec{\nabla} \rho_g \frac{k_{rg}(S_g)}{\mu_g} K(\vec{\nabla} (p_l + p_c(S_g)) - \rho_g \vec{g}) = R_g \qquad (12)$$

- Capillary pressure $p_c$ and relative permeabilities $k_{rl}$, $k_{rg}$ (empirical)
- Gas-density : $\rho_g = f_{EOS}(T, p, y_i) \rightarrow$ **coupling with gas transport !**
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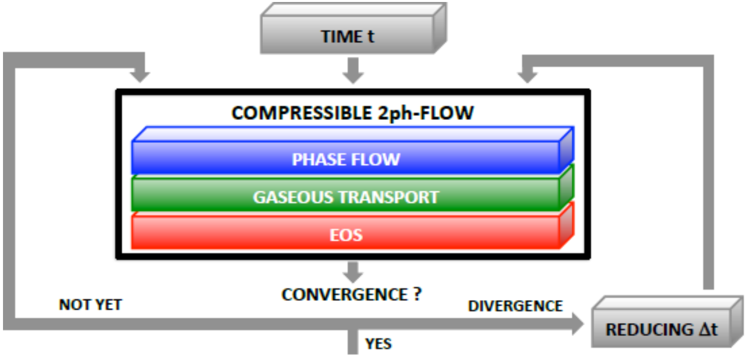
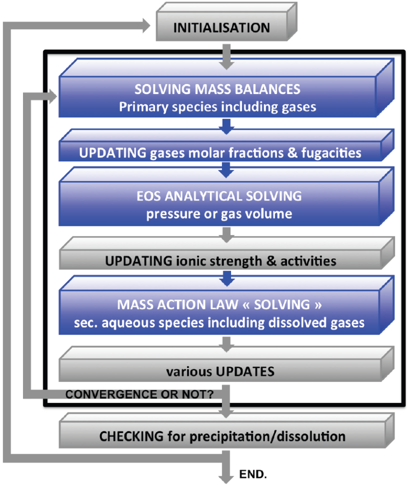
# HYTEC the two-phase flow algorithm



Basis / secondary - species approach :

- Basis-specis $i$, total concentration $= T_i = \sum_{j=1}^{N} \alpha_{ij} c_j$
  - ex : $Tot\ Ca = Ca^{2+} + CaOH^{+} + Portlandite$
  - ex : $Tot\ H = H^{+} - OH^{-} - 2\,Portlandite - CaOH^{+}$
- Activity of species $i = a_i = \gamma_i c_i$ with $\gamma$ : activity coeff
- Thermodynamic equilibrium : Mass action laws with $K_i$
  - Aqueous j : $c_j = \frac{1}{\gamma_j K_j} \prod_{i=1}^{N-basis} a_i^{\alpha_{ji}}$
  - Mineral j : $a_j = 1 = \prod_{i=1}^{N-basis} a_i^{\alpha_{ji}}$
- Gas : activity-fugacity approach (Henry constant : H(T,p))
  - Fugacity coefficient $= \varphi_i = f_{EOS}$,
  - Molar fraction in gas/aqueous phase $= y_i/x_i$ : $\gamma_i x_i H(T,p) = \varphi_i y_i p$

CHESS algorithm with gas : mass-conservation




→ Returns the immobile/mobile/gaseous concentration (for transport)

Iterative - sequential approach (fixed-point)

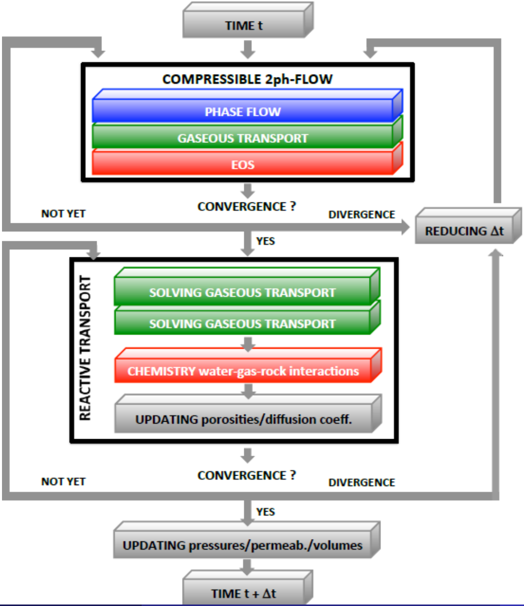
- Transport of the mobile species (linear equation)
- Chemical equilibrium (solid/liquid/gas) on each node

$$\begin{cases} \frac{\partial \omega S_l c_i}{\partial t} = \vec{\nabla}(D_{el}(\omega, S_l)\vec{\nabla} - \vec{u_l})c_i + R_l(\bar{c}, \bar{s}, \bar{g}) & \textit{for Aqueous species} \\ \frac{\partial \omega S_g g_i}{\partial t} = \vec{\nabla}(D_{eg}(\omega, S_l)\vec{\nabla} - \vec{u_g})g_i + R_g(\bar{c}, \bar{s}, \bar{g}) & \textit{for Gas species} \end{cases} \quad (13)$$

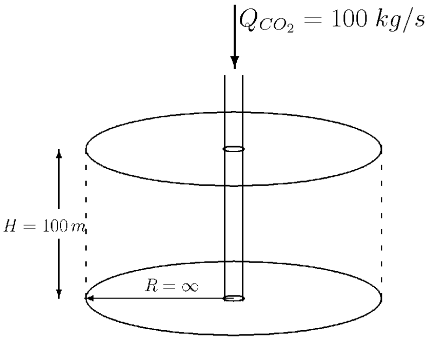
- 2-ph flow provides : Saturation $S_i$ and darcy-velocities $\vec{u_i}$
- Effective Diffusion-coefficient $D_{ei}$ : Archie's law, Millington-Quirk, ...
- Chemistry computes reaction terms $R_i$ ( ... and porosity $\omega$ ?)

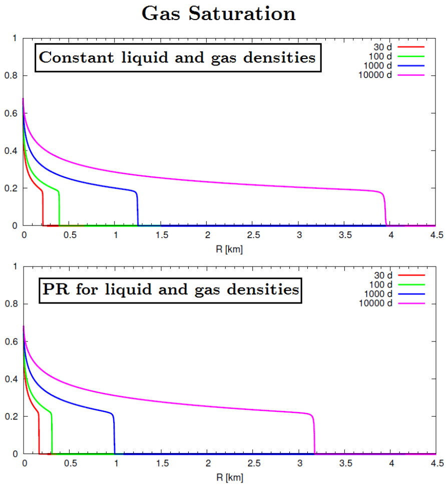
$\rightarrow$ Convergence : $max_{i,node}(||\omega^{(N)} s_i^{(N)} - \omega^{(N-1)} s_i^{(N-1)}||) < tolerance)$

# HYTEC the two-phase flow algorithm



Study of a 1D $CO_2$ injection (100 kg/s) in a saturated aquifer :

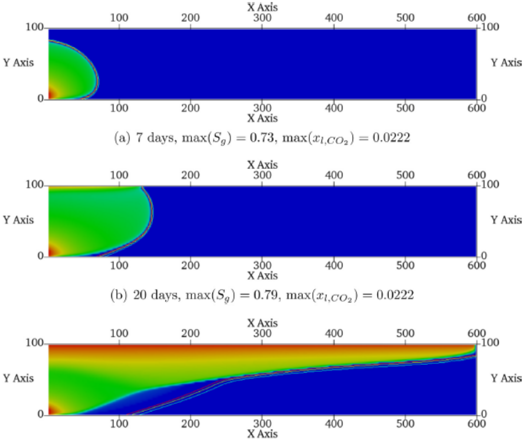



I. Sin et al, 2017, Advances in Water Resources.

# 2D injection and chemistry impact

Study of a $CO_2$ (75%) and $H_2S$ (25%) injection (40 kg/s) in a saturated gas reservoir at 3.1 km depth using Peng-Robinson Model :



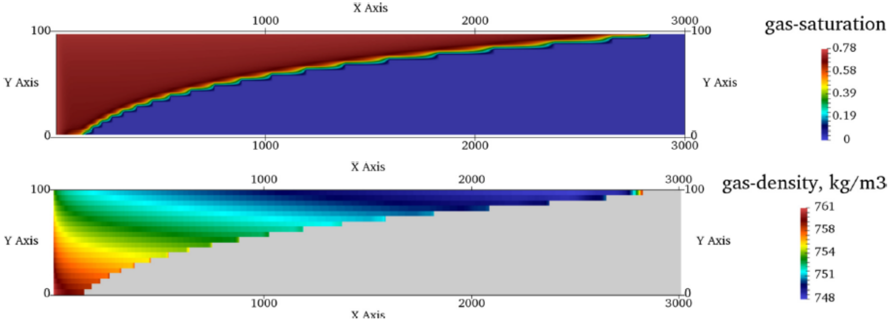

(a) 7 days, $\max(S_g) = 0.73$, $\max(x_{l,CO_2}) = 0.0222$

(b) 20 days, $\max(S_g) = 0.79$, $\max(x_{l,CO_2}) = 0.0222$

(c) 65 days, $\max(S_g) = 0.84$, $\max(x_{l,CO_2}) = 0.0221$

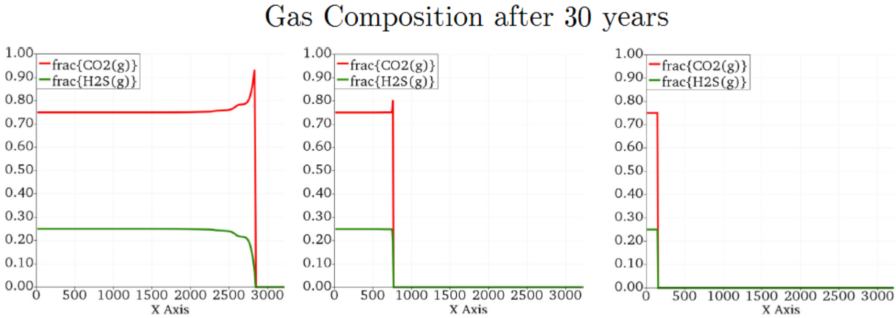
I. Sin et al, 2017, Advances in Water Resources.

Results for the gas phase after 30 years



# 2D injection - results for the gas phase

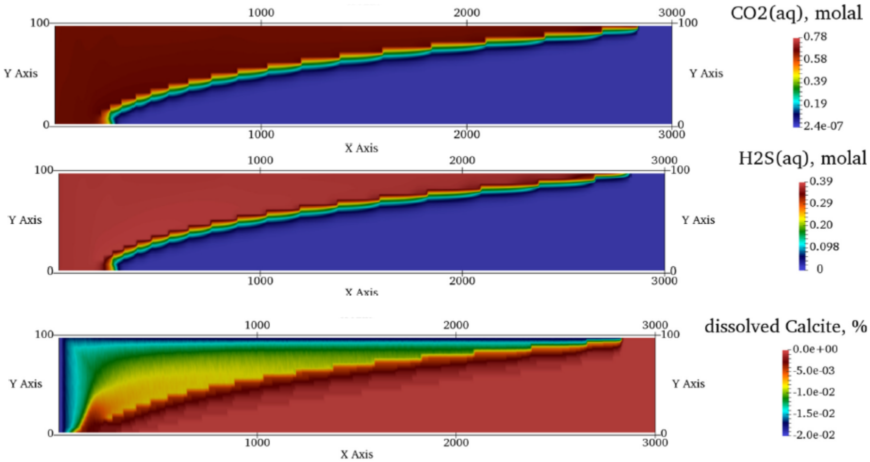
Results for the gas phase after 30 years : chromatographic effect



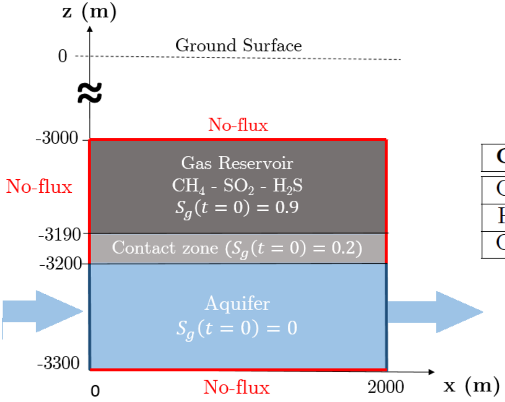

(a) 97.5 m (b) 47.5 m (c) 2.5 m

$\rightarrow$ $H_2S$ more soluble than $CO_2$

Aqueous chemistry results after 30 years



Benchmark : Gas mixture reservoir over an active aquifer



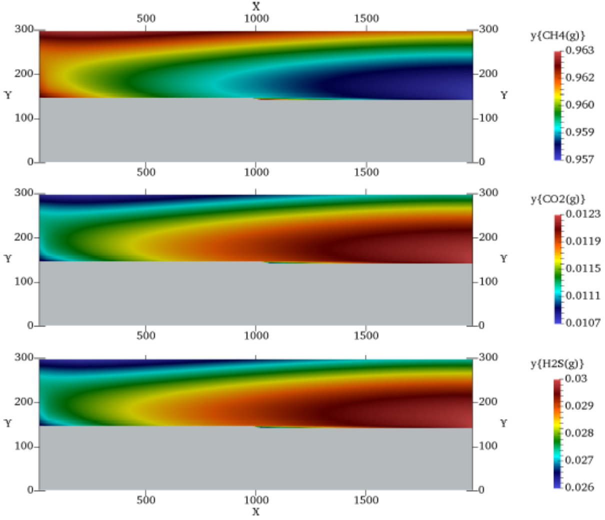

Initial gas reservoir content

| Gas | Molar fraction (%) | Fugacity |
|---|---|---|
| $CH_4$ | 80 | 240 |
| $H_2S$ | 15 | 45 |
| $CO_2$ | 5 | 15 |

- Increasing levels of complexity : convection of gas phase ; EOS ; geochemistry ; ...

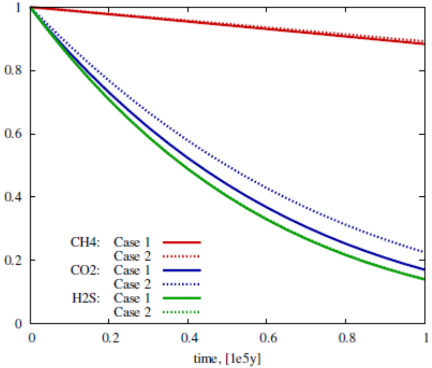
# Ongoing - gas reservoir benchmark

Benchmark : Gas mixture reservoir over an active aquifer without gas convection (study of pure effect of differential gas solubilities)



# Effect of aqueous chemistry

Evolution of the (normalized) amounts of each gas without (case 1) and without (case 2) Calcite :




1. Preferential leaching of $H_2S$ (more soluble)
2. Presence of calcite decreases dissolution of $CO_2$

# Overview of the presentation

# Coupling with porosity

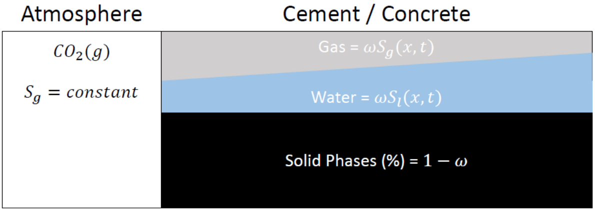
- Dealing with variable porosity has always been a challenge for reactive transport community
  - Intrinsically linked to volume modifications → dilution / concentration
  - How to deal numerically when the volume is not filled (Gas phase ? Pressure decrease ? source term ?)
- For two-phase flow, the chemical equilibrium has to be computed either for constant volume or pressure
  - Is volume really constant ?
- The idea is to incorporate the porosity and the mass of water in the chemistry solver
  - Historically, porosity was corrected after the convergence
- In different applications, the modifications of porosity and the consumption of water (// its activity) have a high impact
  - Cement hydration, atmospheric carbonation of concrete

Atmospheric Carbonation of Concrete was assessed to be one of the main safety issue for the long-term storage of radioactive waste

# The case of atmospheric carbonation

Atmospheric Carbonation of Concrete was assessed to be one of the main safety issue for the long-term storage of radioactive waste

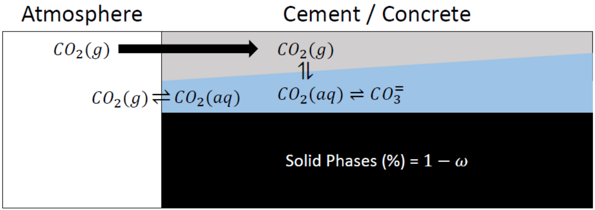
It is a fully coupled problem : 1. Drying of the material - two-phase flow problem




$$\begin{cases} \frac{\partial \omega (1-S_g)\rho_l}{\partial t} - \overrightarrow{\nabla} \rho_l \frac{k_{rl}(S_g)}{\mu_l} K(\overrightarrow{\nabla} p_l - \rho_l \overrightarrow{g}) = R_l \\ \frac{\partial \omega S_g \rho_g}{\partial t} - \overrightarrow{\nabla} \rho_g \frac{k_{rg}(S_g)}{\mu_g} K(\overrightarrow{\nabla} p_l + (p_c(S_g)) - \rho_g \overrightarrow{g}) = R_g \end{cases} \quad (14)$$

# The case of atmospheric carbonation

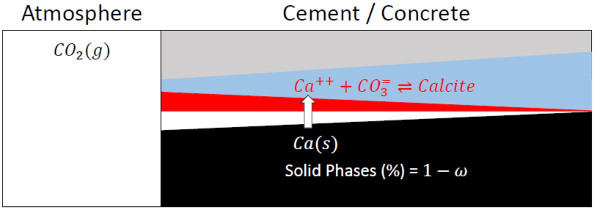
2. Aqueous + gaseous transport and liquid / gas equilibrium




- Advection in both phases : $\overrightarrow{u_i} = \frac{k_{ri}}{\mu_i} K(\overrightarrow{\nabla} p_i - \rho_i \overrightarrow{g})$
- Diffusion in both phases $D_g >> D_l$

$\rightarrow$ Impact on gas pressures, gas-molar fractions, temperatures and densities

3. Solid dissolution and precipitation

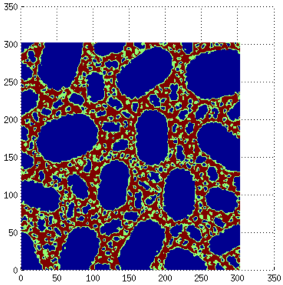


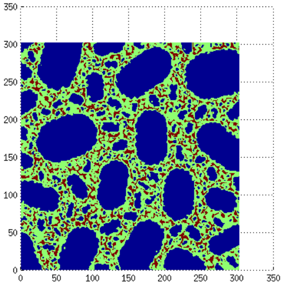

- Calcium reacts with Carbonates to form calcite
- Calcium phase dissolve to provide Calcium and release water
- Important modification of the pore structure : important impact on transport properties

$\rightarrow$ Impact on porosities, saturations, transport properties

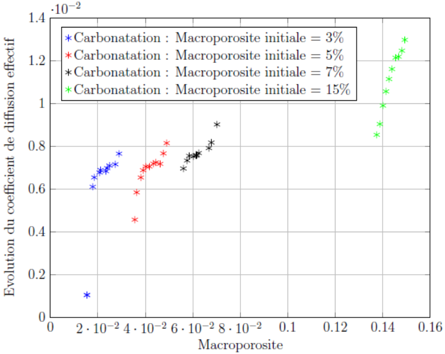
# The case of atmospheric carbonation

- Benchmarking assesses the ability of the codes to solve the equations
- However, not a proof that the results are physically accurate !
- **Question 1** : Are empirical models (Books-Corey, Van Genuchten ?) for $k_{rl}$, $k_{rg}$, $p_c$ relevant able to represent the water distribution within the pore structure ?



- **Question 2** : Are empirical models (Archie, Kozeny-Carman, Millington-Quirk) for diffusion coefficient/permeability able to represent the evolution of the transport properties ?




Seigneur et al, Physics and Chemistry of the Earth, 2017

# Benchmark description

Atmospheric carbonation of concrete : Benchmark exercise between different reactive transport codes (Toughreact, Hytec, Crunch).

1. Drying : comparison between codes (Richard's equation and two-phase description)
    - Richard's equation
    - Full diphasic flow
2. Carbonation at constant saturation and constant porosity
    - Simplified or complete concrete
3. Full problem : need to specify
    - water consumption by chemistry ?
    - variable porosity ?
    - simplified concrete ?

# Overview of the presentation

# Conclusions

- Applications of reactive transport modelling are widespread and the modelling of gas is becoming more and more common
- HYTEC is one of the leading reactive transport code when dealing with gases and multiphase flow problems
  - Thanks to the developments of J. Corvisier and I. Sin in HYTEC
- Still room for improvements : variable porosity and water consumption
- A lot of perspectives : benchmark exercises - focus on two different applications :
  1. Gas reservoir : high pressures and strong dependence on EOS
  2. Atmospheric carbonation of concrete : strong impact of porosity modifications from the complex solid/liquid/gaseous equilibria

**Thank you for your kind attention ! :)**