Thermochemical-based poroelastic modelling of salt crystallization, and a new multiphase flow experiment: how to assess injectivity evolution in the context of CO_2 storage in deep aquifers

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Soutenance de thèse

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CO₂ emissions and CCS: context of the study

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Conclusion and perspectives

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- 5 Conclusion and perspectives

Carbon dioxide and greenhouse effect



Sources: Distangen university college in Canada. Department of geography, University of Dufant, school of geography, United States Environmental Protection Agency (EPA). Washington: Chinas change 1995. The science of climate change, contribution of working group 1 to the second assessment report of the integrovermental panel on climate change. (MEP) and VMD, Chandroa university reveals. (1996).



Marland, G., T.A. Boden, and R. J. Anders. 2007. Global, Regional, and National CO2 Emissions. In Trends: A Compandium of Data on Global Change. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Univel States Dapartment of Enropy, Galk Ridge, Tenn, U.S.A.

International decisions

Several countries (including European Union) agreed to reduce their greenhouse gases emissions (Rio de Janeiro 1992, Kyoto 1997 ...)

CCS: CO₂ Capture and Storage



One of the best mid-term solution to decrease CO_2 emissions is CCS (Carbon dioxide Capture and Storage). With this solution, several billions of tons of emissions could be avoided

- Capture of the CO₂ in the exhaust fumes of the emitters (power plants, cement plants)
- Conditioning and transportation of the CO₂
- Underground injection of the CO₂ in geological formations: deep saline aquifers, coal veins, depleted gas and oil reservoirs



Different pilot projects across the world

Weyburn



source: co2sink.org

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Characteristics of a deep saline aquifer: the example of the Dogger aquifer of the Paris Basin (DPB)

- Geological formation containing highly salted water
 - Classic ions: Na⁺, Cl⁻, Ca²⁺, SO₄²⁻
 - Salinity often higher than seawater: unsuitable for human consumption
- High pressure and temperature
 - 18MPa and 75°C for the DPB
- Constitutive rocks
 - ullet Sandstones: low chemical reactivity, high K and ϕ
 - $\bullet\,$ Limestones: high chemical reactivity, high K and $\phi\,$
- CO₂ under supercritical conditions
 - $\bullet~>$ 7.38 MPa & 31.1 °C
 - high density and low viscosity



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Characteristics of a deep saline aquifer: the example of the Dogger aquifer of the Paris Basin (DPB)

Pore size distribution of rock cores from the DPB

Measured at Laboratoire Navier



Evolution of the aquifer during injection: Flow Through Drying (FTD)

Multiphase flow: CO₂ displaces brine from the pores

- Partitioning almost instantaneous
- CO₂ replaces brine in the pores: apparition of a displacement front



Evolution of the water saturation in the aquifer

Evolution of the aquifer during injection: Flow Through Drying (FTD)



Measured relative permeability curve for the Grès des Vosges

Residual brine saturation

Brine being the wetting fluid, when k_w^r reaches 0, S_w is non 0 (as high as 0.45)

THMC Behavior

Evolution of the aquifer during injection: Flow Through Drying (FTD)



Hydrodynamic regime: viscous fingering

Behavior dominated by viscous forces: \rm{CO}_2 can only penetrate the pores with the lowest hydraulic resistance: the largest pores

Evolution of the aquifer during injection: Flow Through Drying (FTD)

Three kinds of residual water

- Bulk water
- Capillary trapped water
- (Wetting film)



Evaporation of the brine by the continuous supply of carbon dioxide

- Small time scale: evaporation of capillary trapped water
- Long time scale: evaporation of bulk water

Evolution of the aquifer during injection: Flow Through Drying (FTD) Consequences of the evaporation

- Evaporation concentrates the solution and leads to the precipitation of salt
- Addition of solid matter in the porosity
 - Clogging of the percolation paths
 - Creation of stress on the porous matrix: crystallization pressure



How to apply the knowledge of crystallization pressure in the CCS context ?

source: G.W. Scherer

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The stability of small crystals

A small crystal is at a higher pressure than the surrounding solution

 $p_s = p_l + \sigma \kappa_s$



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Modification of the equilibrium: Gibbs free energy for an anisobaric reaction $\Delta_r G = 0 = \Delta_r G^0(p_l, T) - \upsilon_s(p_s - p_l) + RT \ln Q_r$

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Ostwald-Freundlich equation

- $\sigma\kappa_s = \frac{RT}{v_s} \ln S \rightarrow$ the smaller the crystal, the more soluble it is
- S is the supersaturation: $S = \prod_{i} \frac{a_{i}^{\nu_{i}}}{\kappa_{s}(p_{i},T)}$



If the crystal is out of interaction it will keep the shape corresponding to the current supersaturation



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Once the crystal approaches the pore wall its shape is modified



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Interaction of two solid surfaces

When two solid surfaces are put close together

- Overlap of the molecular interaction energy profiles
- Creation of a disjoining pressure



- Bringing the two surfaces close together creates a layering of the solvent molecules
- The ordering and layering of the solvent molecules is the cause of the repulsion force



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Interaction of two solid surfaces Supersaturation and distance between surfaces

The thickness of the film results from the competition between the crystal growth and the repulsion

- ullet Crystal growth tends to fill the gap \rightarrow depends on the supersaturation $S=\frac{1}{p}$
- disjoining pressure tends to increase the gap by destabilizing the crystal \rightarrow Modification of the pressure of the crystal: $\mu_s = \mu_s (p_l + \omega_p)$

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The disjoining pressure is a function of the supersaturation and on the equilibrium thickness

•
$$\omega_p(\delta) = \frac{RT}{\upsilon_s} \ln S$$

•
$$\omega_p(\delta) = \frac{\mathfrak{S}}{\lambda_0} \exp\left(-\frac{\delta}{\lambda_0}\right)$$

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Complete filling of the gap

- The repulsion depends on the intensity of interaction between the surfaces
- Existence of a supersaturation above which the growth is stronger than the repulsion: disparition of the gap and of the disjoining pressure (Mercury, Spiers)

In-pore growth of crystals: crystallization pressure

Thermodynamic combination of the curvature and the disjoining pressure

- the crystal pressure is homogeneous
- $p_s = p_l + \sigma \kappa + \omega_p$





Global form of the crystallization pressure

 $\omega_{p} = rac{RT}{v_{s}} \ln S - \sigma \kappa_{confined}$

In-pore growth of crystals: crystallization pressure

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Global form of the crystallization pressure $\omega_p = \begin{pmatrix} RT \\ v_s \end{pmatrix} \text{ In } S + \sigma_{\kappa_{confined}} \text{ equilibrium of the confined part}$

equilibrium of the free part: Ostwald-Freundlich

In-pore growth of crystals: crystallization pressure conclusion on crystallization pressure

- Apparition of the crystallization pressure when the crystal becomes confined
- The value of crystallization pressure is conditioned by the pore size and the supersaturation
- \bullet Importance of the kinetics of precipitation \rightarrow what about transient supersaturations ?
- Stress effectively transmitted to the pore wall: $p_s^* = \omega_p + p_l$

Poromechanical calculation

Hypotheses

- Small deformations
- Isothermal behavior
- 1D problem

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Elastic energy stored in the matrix

- b Biot coefficient
- N Biot modulus
- K Bulk modulus
- μ Shear modulus

$$W = \frac{1}{2} \left(\frac{b^2}{K + (4/3)\mu} + \frac{1}{N} \right) \left(\sum_J S_J \left(\boldsymbol{p}_J^* - \boldsymbol{p}_{J,0}^* \right) \right)^2$$
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Equivalent tensile stress to reach this elastic energy

$$arpi = \sqrt{2\left(\mathcal{K}+rac{4}{3}\mu
ight)} = \sqrt{b^2 + rac{\mathcal{K}+(4/3)\mu}{N}}\sum_J S_J\left(p_J^*-p_{J,0}^*
ight)$$

Crystallization process



Small time scale

Right after percolation, fast evaporation of the capillary trapped brine

- \bullet fast process \rightarrow importance of the nucleation/growth kinetics
- small quantity of crystal but high transient stresses

Crystallization process



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Crystallization process



Long time scale

Penetration of CO₂ in smaller and smaller pores

- $\bullet\,$ slow process $\rightarrow\,$ can be approximated by an equilibrium situation
- high quantity of crystal but small stresses
- clogging of the pores and decrease of the permeability

Evaporation of capillary trapped brine



Modelling of the brine capillary trapped in a triangular corner

- Calculation of the nucleation and crystal growth under constant evaporation
- Creation of the crystallization pressure when the crystals are confined by the moving meniscus



Evaporation of capillary trapped brine



Evolution of the supersaturation in the corner with time

Crystal and equivalent tensile stress

- Phase 1: no crystal is present
- Phase 2: nucleation and crystal growth \rightarrow consumption of the supersaturation
- Phase 3: Ostwald ripening

Evaporation of bulk brine

Hypotheses: long time scale

- constant concentration: as soon as the crystal nucleates, concentration remains constant in the brine
- equilibrium situation: we consider that at each brine saturation, the crystal is in equilibrium with the current supersaturation
- CO₂ restricted to the biggest pores
- Crystals grow only in brine occupied pores
- $\bullet~\mbox{Ostwald}$ ripening $\rightarrow~\mbox{big}$ crystals are more stable than small crystals

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- \bullet Ostwald ripening \rightarrow big crystals are more stable than small crystals

Crystal will precipitate in the transition pore: the biggest pore filled with brine when the supersaturation is high enough to nucleate

Evaporation of bulk brine



$$S_s(S_w) = rac{
ho_w v_s}{M_s} rac{t_lpha}{
u_lpha} S_w^0 \left(1 - rac{S_w}{S_w^{prec}}
ight)$$

Ion		Na^+	CI⁻
	Fontainebleau	1.794	2.4850
Concentration (g/kg)	Ketzin	90.400	139.000
	Snøhvit	56.418	96.418
	In Salah	35.500	110.250



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Case without salt



$$\varpi = \sqrt{b^2 + rac{K + (4/3)\mu}{N}} \left(S_l \left(p_l - p_l^0 \right) \right)$$

Evaporation with salt



Precipitation increases the volume of $S_l + S_s$ and thus the impact of liquid pressure

• negative difference \rightarrow crystallization pressure does not compensate the volume increase

Evaporation with salt



Precipitation increases the volume of $S_l + S_s$ and thus the impact of liquid pressure

- negative difference \rightarrow crystallization pressure does not compensate the volume increase
- ullet positive difference ightarrow crystallization pressure is bigger than the compressive liquid pressure

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Soutenance de thèse

Conclusion on the modelling of the crystallization pressure

- Pattern of residual saturation and pore distribution influence strongly the behavior
- Two different crystallization processes at two different time scales
 - At small time scale, high transient stresses
 - $\bullet\,$ At long time scale, small equilibrium stresses $\rightarrow\,$ equilibrium hypothesis is a lower bound for stress
- Poroelasticity allows to calculate macroscopical deformations which can be experimentally measured

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How can we experimentally study the evolution of injectivity during drying-out ?

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Original prototype for reactive percolation of supercritical carbon dioxide with (σ ,p,T) conditions

- Flow rate or pressure controlled injection
- Triaxial cell
 - up to 300 bar
- Controlled temperature
 - up to 150°C
- LVDT to measure axial deformation

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Objectives

- Measure the evolution of relative and intrinsic permeabilities during the injection
- Measure the axial deformation of the rock core and identify the different phenomena: capillarity/crystallization

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Additional measurement

- X-ray μ CT before and after experiment
- SEM observation of crystallization pattern at the pore scale





Thanks to David HAUTEMAYOU and Cédric MEZIERE for their help

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Soutenance de thèse

Issues and solutions

Original prototype \rightarrow problems

- Gasometer leakage
- Back pressure valve oscillations
- Phase separator

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External precipitation and clogging of the tubings

- after desaturation, droplets remain in the tubings
- drying and precipitation in these droplets
- clogging of the tubings
- $\rightarrow\,$ Dismounting of the rock core after saturation/desaturation and cleaning of the tubings with pure water

Some possibilities of the set-up Measurement of relative permeabilities

Comparison of the relative permeabilites of a rock core with supercritical and gaseous CO₂

For highly permeability materials, the relative permeabilities are identical



Some possibilities of the set-up

Measurement of capillary pressure



Capillary pressure curve CO_{2g}/water and van Genuchten fit

The dotted line is the van Genuchten fit obtained with the relative permeability measures

Finally, some drying-out results

Experimental conditions

- \bullet Injection of gaseous carbon dioxide 5cc/min at 60°C and 55 bars for 8 days
- Halite concentration at 150 g/L

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Clogging by precipitation

 $150mD \rightarrow 90mD$ 0.8g of salt in the rock core

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 - clogging of the percolation paths
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 - clogging of the percolation paths
 - stress and possible fracturation due to crystallization pressure
- The modelling of the drying of a porous medium allows to differentiate two time scales of precipitation
 - $\bullet\,$ small time scale: evaporation of capillary trapped water $\to\,$ high transient stresses but small crystal quantity
 - $\bullet\,$ long time scale: evaporation of bulk water $\rightarrow\,$ low stresses but high crystal quantity

Conclusion

- Important precipitation of salt is to be expected during the injection of carbon dioxide in deep saline aquifers
 - clogging of the percolation paths
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 - $\bullet\,$ small time scale: evaporation of capillary trapped water $\to\,$ high transient stresses but small crystal quantity
 - $\bullet\,$ long time scale: evaporation of bulk water \rightarrow low stresses but high crystal quantity
- Succeeded to solve numerous issues raised by the permeameter to obtain:
 - comparison of the relative permeabilities to supercritical and gaseous CO₂
 - measurement the capillary curve and relate it to the relative permeabilities
 - first drying-out experiment with encouraging results

Perspectives

Continue the drying-out measurements

- variation of the experimental parameters
 - temperature
 - back pressure
 - CO₂ flow rate
 - brine composition and concentration
- μCT and SEM
- results expected on
 - clogging
 - damage and crystallization pressure
 - measure of axial deformation

Perspectives

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 - clogging
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Microfluidic experiments

- measure in-situ crystallization pressures
- study the residual water pattern and evaporation/precipitation processes