Long term fate of CO$_2$, fluid-rock interactions

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Why looking at “long term” issue?

- Acidic CO$_2$ directly impacting geological environment

1. Long term reservoir and caprock interactions affecting poro/perm

2. Near well environment
   Cement degradation, cement host rock interactions affecting injectivity

3. Leakage enhanced by CO$_2$ driven mineral dissolution (well, fault)

Gaus et al. (2010) modified from IPCC(2007)
What is « long term »?

- Long term assessment of slow geochemical reactions required (~ thousands year)
- Experiments of maximum 20 years on relatively small scale are feasible
- Industrial/natural analogues study though it can differ from CO2 storage
Outlines

- **Case studies on modeling**: the Long Term of Structural/ Dissolution/ Residual/ Mineral (LT SDRM) trapping
  - IPCC Chart representation
  - Uncertainty on mineral trapping magnitude
  - Effect of salinity
  - Influence of others…
First paper on LT SDRM trapping modeling

Title: Reactive geochemical transport simulation to study mineral trapping for CO2 disposal in deep arenaceous formations
Author(s): Xu, TF; Apps, JA; Pruess, K
Source: JOURNAL OF GEOPHYSICAL RESEARCH-SOLID EARTH
Volume: 108 Issue: B2 Article Number: 2071

1D radial geometry
100 kg/s (3.16 Mt/year for 100 years)

CO2 flushes water with piston-like process
Buckley Leverett profile
Gulf Coast Sediment (sandstone)
TOUGHREACT

Figure 2. Water saturations at different times for the 1-D radial flow problem.
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Figure 4. Cumulative CO2 sequestration in different phases after 10,000 years.

Figure 5. Total CO2 sequestered in the three phases for the entire reservoir.
Figure 5. Total CO₂ sequestered in the three phases for the entire reservoir.

- Nice fit with the IPCC 2005 chart
- Except for the residual trapping mechanism
- But 1D model limits the role of the gravity effect
The Sleipner CO2 storage project

Opérateur : Statoil
1 Mt CO₂ / an

2D model
Radial geometry
2D model of CO$_2$ injection at Sleipner
(Audigane et al., 2007, Am. J. of Sc)

vertical 2D mesh with a cylindrical geometrical configuration, centered around an injection point located 155 m beneath the top, 184 m thick formation

Four sand layers of 25 m thickness separated by shale layers of 5 m thickness

At the bottom: sand layer of 70 m thickness into which the CO$_2$ is injected

The first cell has a radius of 10 m, and is followed by 20 cells with radial increments increasing in logarithmic progression out to 100 km from the injection point, so that the model system would be infinite acting.
SHORT TERM SIMULATION RESULTS

- The gas bubble representing the supercritical CO2 extends laterally about 300 m away from the injection point, consistent with the seismic observations.

- The presence of the four intra-shale aquifers gives rise to CO2 accumulations at four different depths and slows the upward migration of CO2.

- The dissolution of gas in the brine produces a maximum dissolved CO2 mass fraction of 0.052.

Gas saturations (SG) and mass fractions of dissolved CO2 in the liquid phase (XCO2L), after 25 years of injection.
> After injection, the upward migration of the CO$_2$(sc) occurs quickly, and most of the CO$_2$ accumulates just below the cap rock, except for the residual CO$_2$ that is trapped in sediments.

> The CO$_2$ plume extends to a maximum radius of 2,000 m around the injection point.

> CO$_2$ starts to dissolve in the brine, and the free gas is completely dissolved after 6,000 years.

> The brine with dissolved CO$_2$ tends to migrate downward as it has approximately 10 kg/m$^3$ larger denser than brine without CO$_2$. The brine containing dissolved CO$_2$ is carried downward and is replaced by brine with less CO$_2$.

> After 10,000 years, a large volume near the bottom of the formation contains brine with dissolved CO$_2$ out to a radius of 4,000 m.
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Mineral Trapping

Precipitation of calcite in the shales: consequence of sand-shale cross-flow

Second CO2 trapping reaction: alteration of albite, leading to the formation of dawsonite and chalcedony

Alteration of chlorite consuming calcite and resulting in the trapping of CO2 into siderite and dolomite

Muscovite dissolution favors albite and chlorite dissolution
- All carbon dioxide present as a free (supercritical) gas phase dissolved
- Dissolution trapping plays a major role in the long term,
  while mineral trapping is minor at 10,000 years (after?)

- 2D model: acceleration the solubility, delays(?) the mineral trapping?
Long-term variations of CO2 trapped in different mechanisms in deep saline formations: A case study of the Songliao Basin, China

Fig. 4 – Schematic representation for the 2D radial model.

Fig. 11 – Time evolution of the injected CO2 in different trapping mechanisms (base-case).

Courtesy of Peter Frykman, GHGT10
IPCC Chart comparison

Gulf coast sediment, US

100 kg/s for 100 y = 316Mt
50% of Quartz

Sleipner Norway

30 kg/s for 25 y = 24Mt
75% of Quartz

Songliao China

50 kg/s for 100 y = 158Mt
25% of Quartz

- Difference in the total amount injected would explain the observed delays in the SDRM trapping estimate
- Mineral trapping difference is more complex to explain as it is an integration of many intercorrelated chemical reactions but inert Quartz amount may play a role
Uncertainties in long term coupled models

**Songliao China sandstone (Zhang et al., 2009)**

- Kinetic rate of chlorite
- Different mineralogical composition

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**Fig. 16** – Comparison of time evolution of the injected CO$_2$ in different trapping mechanisms for three reaction rates of chlorite.

**Fig. 17** – Comparison of time evolution of the injected CO$_2$ in different trapping mechanisms for sensitivity analyses to different mineral compositions.
Uncertainties in long term coupled models

- Coupled modelling papers for the CO₂ injection in the Utsira sands (Sleipner case)


Comparison of outcomes on long term coupled THC modelling studies

<table>
<thead>
<tr>
<th>Reference</th>
<th>Major conclusions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Johnsson et al. (2001, 2004)</td>
<td>Intra-aquifer shales extend the volumetric extent of plume-aquifer interaction, 85% remains as SC-CO₂, 15 % dissolves and &lt;1% precipitates in the near field environment after 20 years. Important reduction in microfracture porosity in the caprock.</td>
</tr>
<tr>
<td>Frangeul et al. (2005)</td>
<td>After 6000 years 55% of the CO₂ in dissolved form, 42 % in ionic form, none precipitated because use of Calcite and Dolomite only</td>
</tr>
<tr>
<td>Thibeau et al. (2007)</td>
<td>Depending on the initial mineralogy, between 40% and 100% of the CO₂ is trapped in minerals after 10000 years.</td>
</tr>
<tr>
<td>Audigane et al. (2007)</td>
<td>95 % of CO₂ dissolved in the brine, 5% taken up by minerals after 10000 years, no sensitivity analysis on the mineralogy</td>
</tr>
</tbody>
</table>
Uncertainties in long term coupled models

Thibeau et al., (2007) assessed the role of non-carbonate mineral (as cation donor) on the mineral trapping CO2 (as carbonate)

- **Run1**: Mg Pathway (Illite->Dolomite)
- **Run2**: Mg and Fe Pathway (+ Annite -> Siderite)
- **Run3**: Mg, Ca, Fe Pathway (+ Anorthite -> Calcium)
Uncertainties in long term coupled models

> Coarse the mesh for longer time scale estimate

![Graph showing CO₂ molar fraction over time](image)

Figure 13: Comparison of fine- and coarse-grid runs

> Over prediction of the solubility due to grid coarsening
Characterisation of secondary minerals

- Dawsonite (NaAlCO₃(OH)₂)

- Included in almost all long term coupled models

- Contributes significantly to the calculation of the trapping capacity

- Observed in certain natural analogues

- Remains unclear if it is a stable phase in a CO₂ storage context

Effect of salinity

Snohvit [2600m, 285bar, 98°C]

Ketzin [600m, 75bar, 36°C (slightly over supercritical cond.)]

In Salah [1850m, 180bar, 96°C]

Sleipner [1000m, 100bar, 37°C]

S = 170 g/L

S = 160 g/L

S = 230 g/L

S = 28 g/L
Using of Pitzer’s model for the high salinity site Ketzin

For a given reaction:

\[ \text{CaCO}_3(s) \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-} \]

Activity \( a \) of the element is defined by the equilibrium constant \( K \)

\[ K = \frac{a_{\text{Ca}^{2+}} \times a_{\text{CO}_3^{2-}}}{a_{\text{CaCO}_3(s)}} \]

Activity coefficient \( \gamma \) is used to account for non-ideal case (high ionic strength)

\[ a_{\text{Ca}^{2+}} = \gamma_{\text{Ca}^{2+}} \times C_{\text{Ca}^{2+}} \]

\[ \gamma_{\text{Ca}^{2+}} = f(I) \]
Effect of Salinity on Calcite dissolution

Fig. 6 – Amount of calcite dissolved in NaCl solutions at 60°C under a $P_{\text{CO}_2}$ of 100 bar calculated with different formalisms (Pitzer, Davies, b-dot).

(Gaus et al., 2008)
Results – initial state @ 36°C at Ketzin

Using Pitzer formalism allow for a better prediction of the initial equilibrium (IS=0) between minerals and brine at Ketzin (before injection)

SCALE2000 (BRGM in house code)
- Pitzer database
- Density calculation (unavailable option in PHREEQC)

PHREEQC (USGS)
- LlnL database (Davies activity model)
- Quintessa database (as received)
- Scale2000 database (BRGM property, confidential)
Effect of dip

Gravity will enhance the residual trapping
Effect of geological heterogeneity

Dissolution of a Stationary CO₂ Plume

Reservoir layer thickness will impact convection cells limiting the solubility trapping

As for heterogeneities!

Audigane, Yamam
Confined system, depleted gas reservoir

CCS and The Netherlands

• Large (clustered) CO₂ point sources (e.g. Rotterdam)

> Large CO₂ potential storage capacity of 3000 Mton (excl. Groningen)
  • 35 aquifers (> 2 Mton)
  • 5 oil fields
  • 131 gas fields (> 4 Mton)

> CO₂ storage in depleted gas fields is less studied than CO₂ storage in aquifers

K12B field
K12B, depleted gas reservoir

- At K12B, the reservoir is a closed system initially 13% of CO2 in the gas phase therefore
  - No mineral trapping,
  - Less solubility trapping
Thank you…
Near Well Zone: Leakage assessment due to FRI
Gherardi, et. al. submitted to Journal Hydrology

Interaction of CO2-charged fluids with cements of abandoned wells, three different domains interacting < reservoir, caprock, cement >, observation point under liquid-saturated conditions, isothermal (@75deg.C) & isobaric (@200 bar) conditions < according to evidences from field: Paris Basin, Dogger & Cox fms >
Assumptions, Simplifications, Limitations

Simplified (and idealized) mineralogy for cement:
< tobermorite instead of other possible amorphous CSH minerals >

Cement minerals ppt/diss reactions modeled under local equilibrium assumpt.

Mass transfer by diffusion in aqueous phase

One single diffusion coefficient for all dissolved species
Geometrical Model

Idealized model, 2-D cartesian geometry,
Rather coarse discretization (dxMIN=dzMIN=0.05 m)
< compromise: 1000 years simulation time >
Geochemical Processes

Chemical driving force mostly provided by gradients in pH and the chemical concentration of CaTOT and CTOT
Main Mineralogical Transformations

Complete obliteration of the initial mineralogy of cement, close to reservoir interface
< effect of the migration of pH-acid, CO2-rich fluids >
Porosity Patterns

Enhanced carbonation at the bottom of the cement domain, near reservoir interface >> porosity clogging >> mechanical integrity ??

Porosity enhancement along the caprock-cement interface

May be of concern ??
< possible fluid escape >
Brine enriched with dissolved CO2 is heavier than the original brine inducing convection and improving dissolution.

Dissolution of CO₂ increases the acidity of the brine, but is buffered by carbonate dissolution.

Maximum decrease of pH is 5.13.
Amount of CO$_2$ stored

![Graph showing the amount of CO$_2$ stored over time. The graph plots Tonnes of CO$_2$ trapped against Time (years). Three types of storage are shown: Mineral, Supercritical, and Dissolved.](image)
Fig. 11 – Time evolution of the injected CO₂ in different trapping mechanisms (base-case).

Wei Zhang a, Yilian Li a,*, Tianfu Xu b, Huilin Cheng a, Yan Zheng a, Peng Xiong a
Long-term variations of CO2 trapped in different mechanisms in deep saline formations: A case study of the Songliao Basin, China

Courtesy of Peter Frykman, GHGT10