Water-rock-\(\text{CO}_2\) interactions for \(\text{CO}_2\) geological storage

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Outline

- Purposes for water-rock-CO$_2$ interaction study
- Typical water-rock-CO$_2$ interactions for CO$_2$ geological storage
- Methods for water-rock-CO$_2$ interaction study
- Future focuses
Purposes for water-rock-CO2 interactions study

- determining CO$_2$ trapping mechanisms in saline formations
- understanding reservoir geochemical responses
- providing geochemical monitoring indicators
- assessing impact of CO2 storage on groundwater systems
- ..................
CO₂ trapping mechanisms in saline formations

Generally, four processes have been identified as the most important CO₂ trapping mechanisms for CO₂ sequestration in saline formations:

- Structural and stratigraphic trapping
- Residual trapping
- Solubility trapping
- Mineral trapping

(IPCC, 2005)

With different time scales, the proportion of different forms of CO₂ trapping mechanisms are varying and for different specific injection reservoir, the proportions of CO₂ trapping mechanisms are specific due to specific reservoir mineral compositions and formation water chemistry.

(Audigane P. et al., 2007)
Generally speaking, after CO2 is injected into deep saline formations, pH of reservoir water will decrease by 1-2 units and concentrations of chemical components like Al, Si, and HCO$_3^-$ increase significantly. And CO2 would be sequestrated (fixed) mainly by secondary carbonate minerals.

(Li et al., 2010)
Minerals in the formation water show different evolution tendency due to specific rock compositions and water chemistry. In Xu’s model, CO2 will be trapped by calcite, dolomite, siderite and dawsonite, which will occur in the presence of high pressure CO2.
(Palandri and Kharaka, 2009)
Providing geochemical monitoring indicators

In order to understand the migration path of CO2 plume and what happens after large volume CO2 is injected into the reservoir, effective monitoring needs to be carried out.

Although geophysical monitoring is very efficient, it’s expensive and is difficult to apply.

Geochemical monitoring is effective if appropriate monitoring indicators are identified.
Results from experiments, field tests and numerical simulation indicate that pH, ion concentrations of HCO3-, Fe, Mn will increase even by magnitudes and these geochemical constitutes can be effective monitoring targets.

(Kharaka et al., 2006)
Isotopes of formation water can be chosen as geochemical indicators since great oxygen-shifts have been observed in CO₂ injection due to isotope exchange between formation water, CO₂, and reservoir minerals.

(Myrttinen et al., 2010), Ketzin test
Investigating impact of CO2 storage on groundwater systems

Once injected, CO2 could accelerate water-rock interaction and cause pH decrease and mobilization of metals and hazardous inorganic and organic constituents which could lead to groundwater quality deterioration. When CO2 migrates from a deep saline formation, e.g. via local high-permeability pathways such as permeable faults or degraded wells, it will arrive in shallow groundwater systems and change the geochemical conditions in the aquifer and will cause secondary effects, contaminating shallow groundwater resources.
Concentrations of major cations in groundwater from the ZERT wells. Note the relatively constant concentrations of Na and K, but the general increases in the concentrations of divalent cations with water alkalinities, possibly indicating dissolution of carbonate minerals.

Results from Research Project on CO2 Geological Storage and Groundwater Resources from Earth Sciences Division, LBNL.
When CO2 is injected into groundwater, concentration of Fe and Mn show an increase.

The low Fe and Mn concentrations during July 20 to July 26 could be attributing to the oxidizing conditions possibly caused by percolating oxygenated water from rainfall events.
Typical water-rock-CO$_2$ interactions for CO$_2$ geological storage

CO$_2$+H$_2$O $\leftrightarrow$ H$_2$CO$_3$ (aq)
H$_2$CO$_3$ (aq) $\leftrightarrow$ H$^+$+HCO$_3^-$
Calcite + H$^+$ $\leftrightarrow$ Ca$^{2+}$+ HCO$_3^-$
Dolomite+ 2H$^+$ $\leftrightarrow$ Ca$^{2+}$+ Mg$^{2+}$+2HCO$_3^-$
Chlorite+ 16H$^+$ $\leftrightarrow$ 5Mg$^{2+}$+2Al$^{3+}$+3SiO$_2$ (aq) +12H$_2$O
Albite + 4H$^+$ $\leftrightarrow$ Na$^{+}$+Al$^{3+}$+3SiO$_2$ (aq) +2H$_2$O
Dawsonite + 4H$^+$ $\leftrightarrow$ Na$^{+}$+Al$^{3+}$+CO$_2$ (aq) +3H$_2$O
Anorthite+ 8H$^+$ $\leftrightarrow$ Ca$^{2+}$+2Al$^{3+}$+2SiO$_2$ (aq) +4H$_2$O

.............
In the Frio test, the observed increases in concentrations of HCO₃ and Ca likely result from the rapid dissolution of calcite (1); the increases of Fe are likely caused by dissolution of the observed iron oxyhydroxides (2), this is the same for Mn; another dominant reaction is aluminosilicate mineral dissolution.

\[
\text{CO}_2(g) + \text{H}_2\text{O} + \text{CaCO}_3(s) \\
\leftrightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-. \quad (1)
\]

\[
8\text{Fe(OH)}_3(s) + \text{CH}_3\text{COOH}^0 + 14\text{H}^+ \\
\leftrightarrow 8\text{Fe}^{2+} + 2\text{HCO}_3^- + 20\text{H}_2\text{O}. \quad (2)
\]

\[
0.4\text{H}^+ + \text{Ca}_{0.2}\text{Na}_{0.8}\text{Al}_{1.2}\text{Si}_{2.8}\text{O}_8(s) \\
+ 0.8\text{CO}_2(g) + 1.2\text{H}_2\text{O} \\
\leftrightarrow 0.2\text{Ca}^{2+} + 0.8\text{NaAlCO}_3(\text{OH})_2(s) \\
+ 0.4\text{Al(OH)}_3(s) + 2.8\text{SiO}_2(s). \quad (3)
\]
The following reactions are proposed to summarize the geochemical processes at Nagaoka during the early stage of CO2 storage at the reservoir (Mito et al., 2008).

\[
\text{CO}_2\text{(supercritical)} \rightarrow \text{CO}_2\text{(aq)}
\]

\[
\text{CO}_2\text{(aq)} + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{HCO}_3^-
\]

\[
\text{Plagioclase} + 2\text{H}^+ + 3\text{H}_2\text{O} \\
\rightarrow \text{Ca}^{2+} + 2\text{Al(OH)}_3 + 2\text{H}_4\text{SiO}_4 + \text{NaAlSi}_3\text{O}_4
\]

\[
\text{Chlorite} + 20\text{H}^+ \rightarrow 5\text{Mg}^{2+} + 5\text{Fe}^{2+} + 4\text{Al(OH)}_3 + 6\text{H}_4\text{SiO}_4
\]

\[
\text{Calcite} + \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{HCO}_3^-
\]
The low pH and under-saturation of the solution promoted extensive calcite cement dissolution in all samples. The overall alterations after the initial acidification and dissolution of carbonates are represented by the following reactions (Ketzer et al., 2009):

\[
2\text{KAlSi}_3\text{O}_8 + 2\text{NaAlSi}_3\text{O}_8 + \text{Ca}^{2+} + \text{CO}_2 + 4\text{H}_2\text{O} \\
\xrightarrow{\text{K-feldspar albite}} \\
2\text{CaCO}_3 + 2\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{Na}^+ + 2\text{K}^+ + 8\text{SiO}_2 \\
\xrightarrow{\text{calcite kaolinite quartz}}
\]
Methods for water-rock-CO$_2$ interaction study

- Experiments of Water-rock-CO$_2$ interactions in laboratory
- Numerical simulation of a specific site
- Field test and corresponding monitoring
Physical modeling of water-rock-CO2 interaction for Nagaoka test site of Japan

Reaction conditions: 50°C and 10MPa;

Reaction time: 15 days;

Reactants: formation water stored for two years and 4g rock powers;

(Mito S. et al., 2008)
Water-rock-CO₂ interaction study for Rio Bonito Formation (Permian), southern Brazil

200 ℃ and 10-15 MPa; 100 h; distilled water and round rock samples; (Ketzer J.M. et al., 2009)
Water-rock-CO2 interaction study for CO2 sequestration in the Guantao formation of the Bohai Bay Basin, NE China

200°C and 20MPa;
15 days;
Formation water and rock;
Methods for water-rock-CO$_2$ interactions study

- Experiments of Water-rock-CO$_2$ interactions in laboratory
- Numerical simulation based on specific site
- Field test and corresponding monitoring
Numerical simulations on specific site

List of numerical codes (Study performed by Geogreen)

## Models at a Glance

<table>
<thead>
<tr>
<th>Name</th>
<th>Affiliation</th>
<th>Developers</th>
<th>Status</th>
<th>Phase transition</th>
<th>Geochemistry</th>
<th>Thermal</th>
<th>Solid matrix Deformation</th>
<th>Discretization method (space)</th>
<th>Discretization method (time)</th>
<th>Wells &amp; Fractures</th>
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<td>Gerritsen</td>
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<td>☐</td>
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<td>☐</td>
<td>Pressure: MPFA Flow, Streamline</td>
<td>MMOC along streamlines</td>
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<td>☐</td>
<td>☐</td>
<td>☐</td>
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<td>☐</td>
<td>Spectral Galerkin</td>
<td>Explicit 4th order</td>
<td>Homogenous medium</td>
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<td>☐</td>
<td>☐</td>
<td>☐</td>
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<td>FD</td>
<td>Implicit</td>
<td>No special treatment</td>
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<td>Integrated FV</td>
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<td>Line source/sink wells</td>
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<td>(Bryant)</td>
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<td>A TOUGH2 module for coupled subsurface-atmosphere transport of water, brine, CO2, 1 tracer, air</td>
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</tbody>
</table>

1 Developers present at workshop. For complete lists, see the questionnaires at the end of this document. Non-developer presenters are indicated with brackets.

2 Green checks (✓) indicate "yes" (or "publicly accessible" for the status column), grey circles () "still in development", and red crosses (✗) "no".
Changes of different kinds of minerals over time scales due to water-rock-CO2 interactions.

(Xu et al., 2006)
(Ketzer J.M. et al., 2009)
(Barbara et al., 2009)
(Zhang et al., 2009)
Methods for water-rock-CO$_2$ interaction study

- Experiments of Water-rock-CO$_2$ interactions in laboratory
- Numerical simulation based on specific site
- Field test and corresponding monitoring
Ions changes and dissolution kinetics of K-feld from the field test of CO2 injection in Nagaoka site.

(Mito et al., 2008)
E. Conductance ($\mu$S/cm)

- $\delta^{18}$O H$_2$O (per mil)
  - $\delta$D H$_2$O (per mil)
- Fe (mg/L)
- Mn (mg/L)

(Kharaka et al., 2006)
Isotope changes results from Ketzin injection site of Germany.

(Myrttinen et al., 2010)
Geochemical background of formation water from Guantao formation, Bohai Bay Basin.
Future focuses

- Water-rock-CO2 interaction for specific reservoir conditions
- Influences of water-rock-CO2 interactions on CO2 storage capacity
- Minerals kinetics in water-rock-CO2 interaction and corresponding influences on reservoir physical properties
Different sedimentary environments can lead to different reservoir and caprock conditions, e.g., continental and marine sedimentary environments.

Different reservoir minerals and formation water chemistry may have great influences on water-rock-CO2 interactions.

Therefore, water-rock-CO2 interaction should be studied for each specific testing site.
CO2 storage capacity is variable and is mainly controlled by the capacities of mineral, solubility, structural and stratigraphic and residual trappings.

The proportion of different trapping forms is changes with time and so does the total capacity.

Attention should be paid to CO2 storage capacity at specific time scales.

(Audigane et al., 2007)
Minerals kinetics in water-rock-CO2 interaction

The general rate equation is adopted from Lasaga et al., 1995 and in general, the most well-studied mechanisms are those in pure H2O (neutral pH) and those catalyzed by H+ (acid) and OH- (base). For many minerals, the full equations include terms for each of these three mechanisms.

\[
A = A^0 \cdot \frac{V_f}{V_f^0} \quad \text{and} \quad A_{geom} = \frac{6}{\rho \cdot d_s}
\]

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a. Arrhenius pre-exponential factor A, mole m^{-2} s^{-1} for use with equation (5).
b. log rate constant k computed from mole m^{-2} s^{-1}.
c. Arrhenius activation energy E, J.
d. Reaction order n with respect to.
e. Calculated using geometric surface area.
f. Calculated by Tester et al. (199).
g. Calculated using BET surface area.
h. Calculated by Tester et al. (1994) using BET surface area.
i. From Knauss and Wolery (1988), A adjusted here from 491 to 10 to be consistent with the results of Tester et al. (1994).

(Transitionary theory by Lasaga et al., 1995)
谢谢！

Thanks！