Dissolution and carbonation of activated serpentine for combined capture and storage

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Outline

- Flue gas mineralization – the concept
- Experimental setup and material
- Capture via mineralization:
  - EQ3/6 equilibrium simulations
  - Dissolution experiments
  - Dissolution model
- Storage via mineralization:
  - EQ3/6 equilibrium simulations
Flue gas mineralization within a CCS system

Traditional approach

after Verduyn et al. 2009, TCCS5, Trondheim
Flue gas mineralization within a CCS system

Novel approach

after Verduyn et al. 2009, TCCS5, Trondheim
Mineralization plant

Key:
- regular capillary
- heated capillary
- isolated from rack by flexible connections

100% CO2
90% N2
10% CO2

30-180°C

and make-up

sample withdrawal

gas analysis (MS)

liquid analysis (IC)

pH probe

to sample collector (& offline analysis)

to vent
Mineralization plant

$P_{CO_2} = 11 - 150$ bar

**Gas phase:**

*100% CO$_2$*

**Temperature:**

30-180°C
Mineralization plant

$P_{CO_2} = 0.36 - 4\text{ bar}$

**Synthetic flue gas:**
$10\%_{vol} CO_2$ in $N_2$

Key:
- regular capillary
- heated capillary
- isolated from rack by flexible connections

30-180$^\circ C$
Activated serpentine

- **Mg$_{2.42}$Fe$_{0.58}$Si$_2$O$_5$(OH)$_4$**
- dry ground to <125 µm
- thermal activation at 600°C
- 1.5 mol H$_2$O per mole serpentine removed

- fractionation by dry sieving
- fines removal w/ EtOH
- micropores (2-3 nm) measured (BET method)
Capture part: EQ3/6 equilibrium simulations

CO₂ solubility as function of T and [Mg²⁺], at different P_{CO₂} levels

**using flue gas (P_{tot} = 10P_{CO₂}):**

- If flue gas used: CO₂ solubility predominately sensitive to [Mg²⁺]
  - even at low P_{CO₂} high CO₂ loads possible

**using pure CO₂:**

- If pure CO₂ used: low T favorable, highest P_{CO₂} not worth the while

\[ P_{CO₂} = \begin{align*} & 4 \text{ bar} \\ & 1.5 \text{ bar} \\ & 0.36 \text{ bar} \\ & 120 \text{ bar} \\ & 60 \text{ bar} \\ & 11 \text{ bar} \end{align*} \]
Act. serpentine dissolution experiments

**Mg$_{2.42}$Fe$_{0.58}$Si$_2$O$_5$(OH)$_4$**

**Magnesium** concentration and conversion at 30°C:

$\rightarrow$ Dissolution using flue gas similarly effective as with pure CO$_2$

$\rightarrow$ Complex dissolution mechanism: Drastic slowdown after fast initial phase
Olivine vs activated serpentine dissolution

$$T = 30^\circ\text{C}, \ P_{\text{CO}_2} = 0.36 \ \text{bar}, \ \text{flue gas mode}, \ 20-63 \ \mu\text{m fraction}$$

→ Olivine so far “best candidate” Mg-silicate (most reactive)*

*e.g. O’Connor et al., 2005, Albany Research Center*
Dissolution model for natural serpentine

Natural serpentine dissolves acc. to Shrinking core model*

- Population balance:
  \[ \frac{\partial n}{\partial t} - \frac{\partial D n}{\partial L} = 0 \]
  \( n = \) particle population, PSD
  \( D = \frac{dL}{dt}, \) dissolution rate

- Dissolution rate:
  \[ D = f \left( L, L_0 \right) \]
  not constant, diffusion controls

- Solute mass balance:
  \[ V \frac{dc}{dt} = \frac{dm}{dt} - Qc \]
  \( c = \) solute concentration
  \( m = \) mass of particle population

*e.g. Teir et al., 2007, Int J Miner Process 83;
Van Essendelft et al., 2009/2010, Ind Eng Chem Res 48/49
Dissolution model for activated serpentine

- Presence of micropores and altered crystal structure cause complex, incongruent dissolution behavior
- \( \text{Mg}_{2.42}\text{Fe}_{0.58}\text{Si}_2\text{O}_5(\text{OH})_4 \rightarrow \text{Silica} \) detected in reactor solution:

![Graph showing Mg and silica concentrations over time at different pressures](image1)

![Graph showing conversion percentage over time at different pressures](image2)
Dissolution model for activated serpentine

- Presence of micropores and altered crystal structure cause complex, incongruent dissolution behavior

\[ \text{Mg}_{2.42}\text{Fe}_{0.58}\text{Si}_2\text{O}_5(\text{OH})_4 \rightarrow \text{Iron} \text{ absent in reactor solution:} \]

\[ T=60^\circ\text{C} \]

\[ \rightarrow \text{Preferential leaching of} \quad \text{Mg}^{2+} \]
Dissolution model for activated serpentine

- Presence of micropores and altered crystal structure cause complex, incongruent dissolution behavior

- Back to single particle model to explore the role of:
  - diffusion
  - counterdiffusion
  - ash layer
  - unreacted core
  - pores
  - reactants (H\(^+\))
  - products (Mg\(^{2+}\), silica)

- PSD discretized to perform preliminary simulations
- Single experiments can be fitted nicely, but fitting multiple experiments yet an issue
Dissolution model for activated serpentine

Measured and modelled Mg²⁺ profile and conversion:

\[ T = 90^\circ C, P_{CO_2} = 0.36 \text{bar, flue gas} \]
Serpentine dissolution experiments

T=30°C

T=60°C

T=90°C
Storage part: EQ3/6 equilibrium simulations

Thermodynamic driving force (Q/K) as function of T and [Mg^{2+}]:

$P_{CO2} = 0.36 \text{ bar, flue gas}$

$P_{CO2} = 60 \text{ bar, pure CO}_2$

$\rightarrow$ Higher T favors carbonate precipitation

$\rightarrow$ High $P_{CO2}$ not beneficial, flue gas conditions preferable!
Concluding remarks

- CO$_2$ capture into aqueous solution promoted by presence of Mg$^{2+}$ from the dissolution process
- Activated serpentine dissolution fast even at low P$_{CO_2}$, thereby preferential leaching of Mg$^{2+}$
- Higher T promotes Mg leaching and reduces carbonate solubility
- Thermodynamic driving force for precipitation higher under flue gas conditions
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Thanks for your attention

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