CO$_2$ fixation by serpentinite

Ron Zevenhoven
Åbo Akademi University, Turku, Finland

Overview

- Background and scope
  - CO$_2$ mineral sequestration
  - The ÅA route for stepwise serpentine carbonation
- Progress / results since 2006
  - Mg(OH)$_2$ production from magnesium silicate-based rock
  - Mg(OH)$_2$ carbonation
  - Process energy requirements
  - Avoid CO$_2$ capture: direct operation on flue gas
- Conclusions
CCUS* in / for Finland

<table>
<thead>
<tr>
<th>Earlier: &quot;CCS&quot;</th>
<th>In Finland</th>
<th>Near Finland / abroad</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geological storage</td>
<td>Not possible</td>
<td>Baltic sea?</td>
</tr>
<tr>
<td>Ocean storage</td>
<td>Not possible</td>
<td>Not possible</td>
</tr>
<tr>
<td>Mineral sequestration</td>
<td>Large potential Projects ongoing</td>
<td>Projects ongoing PT, SG, LT, (CA?, ZA?)</td>
</tr>
<tr>
<td>CO₂ utilisation</td>
<td>Several applications (PCC, CO₂ solvent...) Projects ongoing</td>
<td>Projects ongoing US</td>
</tr>
</tbody>
</table>

*Carbon capture, utilisation and storage, or Carbon capture, use and sequestration

**CO₂ mineralization: what, how**

Overall carbonation chemistry, with \( M = \text{Mg or Ca} \) (or \( \text{Fe, ...} \))

\[
M\text{O}_y\text{SiO}_2z\text{H}_2\text{O} (s) + \text{CO}_2 (g) \iff M\text{CO}_3(s) + y\text{SiO}_2(s) + z\text{H}_2\text{O} (l) + \text{HEAT}
\]
**CO₂ mineralization potential**

- Much **larger potential** than other CCUS options, *for example*:
  - Olivine-containing rock in Oman (350 × 40 × 5 km, ~30% olivine)
  - **Could bind all fossil carbon**
  - Available **world-wide**, hence increasing attention
  - No "leakage" problems from carbonates

---

**CO₂ mineralization potential: Oman**

*Oman: some of the 77 trillion tonnes of ultramafic rocks*

**Pictures:**
- Pictures: R Hunwick
- Presented in Sydney, March 12, 2012

Olivine-containing rock in Oman (350 × 40 × 5 km, ~30% olivine)

*Kelemen & Matter, PNAS 2008*
Mineral resources; source-sink links

For example for Finland:

- Vammala Mg-silicate resources (~200 Mt rock)

- Possible application:
  Meri-Pori power plant
  (2.5 Mt CO₂/y)

Serpentinite materials recently tested, as oxides (%-wt)

<table>
<thead>
<tr>
<th></th>
<th>MgO</th>
<th>CaO</th>
<th>Fe₂O₃*</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hitura (FI)</td>
<td>36.2</td>
<td>0.5</td>
<td>14.4</td>
<td>24.8</td>
<td>&lt;0.1</td>
<td>24.1</td>
</tr>
<tr>
<td>Ni-ore Hitura (FI)</td>
<td>28.5</td>
<td>0.6</td>
<td>15.9</td>
<td>33.9</td>
<td>2.0</td>
<td>19.1 (NiO 1.0)</td>
</tr>
<tr>
<td>Vammala (FI)</td>
<td>19.2–28.0</td>
<td>1.4–90</td>
<td>15.4–18.4</td>
<td>39.3–46.9</td>
<td>1.3–3.5</td>
<td>7.9–11.6</td>
</tr>
<tr>
<td>Suomusjärvi (FI)</td>
<td>13.5–20.9</td>
<td>7.8–8.3</td>
<td>10.9–11.9</td>
<td>44.3–50.2</td>
<td>7.0–10.8</td>
<td>6.8–7.6</td>
</tr>
<tr>
<td>NSW Gt Serp belt (AU)</td>
<td>38.1</td>
<td>0.05</td>
<td>6.9</td>
<td>41.8</td>
<td>1.0</td>
<td>12.1</td>
</tr>
<tr>
<td>Bragança 7 fontes (PT)</td>
<td>35.8</td>
<td>0.02</td>
<td>8.2</td>
<td>41.9</td>
<td>1.2</td>
<td>12.8</td>
</tr>
<tr>
<td>Bragança Donai (PT)</td>
<td>36.7</td>
<td>0.25</td>
<td>7.29</td>
<td>42.7</td>
<td>1.6</td>
<td>11.5</td>
</tr>
<tr>
<td>Varena (LT)</td>
<td>25.5–35.4</td>
<td>0.21–2.5</td>
<td>14.1–33.6</td>
<td>28.8–37.2</td>
<td>0.11–1.8</td>
<td>9.5–15.0</td>
</tr>
</tbody>
</table>

* Calculated, presumably a mixture of FeO and Fe₂O₃, partly (?) Fe₃O₄.
Mg-silicate carbonation: the ÅA route

1. Mg(OH)₂ production
   - Mixing serpentinite and AS
   - Heating (<450°C)
   - Dissolution of MgSO₄ and precipitation of Mg(OH)₂ from aqueous solution
   - Regeneration of AS salt

2. MgCO₃ production
   - Pressurised fluidised bed
   - > 20 bar, > 500°C
   - MgCO₃

Test methods @ ÅA 2007 →
Closed loop process producing Mg(OH)$_2$ from Mg-silicate rock

Specific surface
40 – 50 m$^2$/g

Pore volume
20 – 25 cc/g

Producing Mg(OH)$_2$ from Mg-silicate rock:

Tested:
1) dry / wet samples
2) mixing / no mixing
3) layered / pre-mixed
4) Al / ceramic sample holder
5) Ammonium sulphate/ bisulphate

Nduagu, dr. thesis AA 2012
Summary for Mg(OH)$_2$ production

- **Rock type**
  - Serpentinites (Mg/Fe ratio)
  - Preferably max 400°C

- **Temperature**
  - (°C)
  - 250 to 650

- **Time**
  - (min)
  - >30 to 60

- **Process energy**
  - GJ/t-CO$_2$
  - >3.5 to 6

- **GHG footprint**
  - kg-CO$_2$e/t-CO$_2$
  - 380 to 500

The pressurised fluidised bed @ ÅA

**Research questions:**
1) No build-up of MgCO$_3$ on Mg(OH)$_2$ particles?
2) Fast kinetics?
3) What about supercritical CO$_2$?
Mg(OH)$_2$ carbonation – results
using commercial Dead Sea Periclase material (BET ~ 5 - 8 m$^2$/g)

~ 20 bar CO$_2$ \rightarrow ~ 58 bar CO$_2$

unusually high Mg(OH)$_2$

scCO$_2$: no advantage (tests up to ~80 bar)

DSP Mg(OH)$_2$

Low P: 25 bar, 495°C
High P: 59 bar, 550°C

- Competition between dehydroxylation and carbonation
  - Own-produced Mg(OH)$_2$ has good quality (green triangles)
  - Optimise Mg(OH)$_2$ precipitation conditions, control properties

Fagerlund, dr. thesis ÅA 2012
Process energy requirements

Mechanical vapour recompression (MVR) crystallization of AS salt

MVR compression work ~1.2 GJ/t CO₂

Reaction enthalpies vs. temperature for extraction of 1 mol of Mg from pure serpentine or from Finnish serpentinite, and for the carbonation.

→ Mg(OH)₂ production needs 3 - 4x the heat the carbonation gives

Total penalty ~3 GJ (mainly 400°C heat) and ~3 t rock per ton (1000 kg) CO₂

Optional: application at a lime kiln 2013

Integration lime kiln, no CO₂ capture, full flue gas compression to 80 bar ~ 20 bar CO₂,
0.2~0.25 t CO₂/h fixed,
heat (kiln gas) 2.6 GJ/t, power 0.9 GJ/t CO₂

Slotte et al. 2012/2013
Conversion of Mg(OH)$_2$ to MgCO$_3$ and MgO in (wet) CO$_2$ or CO$_2$ diluted with (26-72%) N$_2$.

**Graphs:**
- MgO-content vs. Mg(OH)$_2$-content for no nitrogen and added nitrogen conditions.
- MgCO$_3$-content vs. Mg(OH)$_2$-content for no nitrogen and added nitrogen conditions.

**Total pressure 10 – 59 bar, temperature 450 - 550°C, time 15 minutes**

Dead Sea Periclase (DSP) Mg(OH)$_2$, 212-425 µm

**Conclusions**
- CO$_2$ mineral sequestration offers a leakage-free alternative for CO$_2$ underground storage worldwide; only option inside Finland
- CO$_2$ capture from oxygen containing gases isn’t ”taking off”: capture is more expensive than economically viable CCUS! → remove capture step from CCUS chain by operating mineralisation directly on flue gas.
- ÅA staged process route: ~ 80 % Mg extraction from serpentinite + fast (~10 min) Mg(OH)$_2$ carbonation ~65%
- Energy input ÅA route so far ~3 GJ/t, ≈ CO$_2$ capture from NG
- Challenge: Mg(rock) → Mg(OH)$_2$ > 90% & ”good” particles
- Several LCA studies have been reported, uses are found for the solid products. For example heat storage in Mg (hydro)carbonate
- Integrate CCUS with flue gas desulphurisation ?!