Dinamica degli inquinanti

Mineral Carbonation

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**Orders of magnitude**

- Atmospheric stock: 2800 Gt CO$_2$ (~760 GtC)
- Worldwide CO$_2$ emissions: 25 Gt/year (~7 GtC)
- Annual accumulation: 15 Gt CO$_2$/y (~4 GtC)
- Exploitable coal reserves: ~1000 GtC (3000 Gt CO$_2$)
- Largest commercial CCS: 1 Mt CO$_2$/y
  (300 MWe gas fired power plant)
Mineral carbonation

\[
\text{MO} + \text{CO}_2 \rightarrow \text{MCO}_3 + \text{heat}
\]

\( M = \text{Calcium, Magnesium, Iron} \)

**Issues**

- stability of carbonates
- availability of alkalinity sources
- reactivity of alkaline materials
Stability of carbonates

Tests performed at 1M CaCO$_3$ / MgCO$_3$ concentration

Ambient temperature – 500 / 300 rpm

Dissolution at rainwater pH: 0.4% (CaCO$_3$) – 0.06% (MgCO$_3$)

Stability of carbonates

Calcium carbonate

- Most of dissolved Mg/Ca remains in solution and a fraction is released as gas.
- Tests performed dissolving 50 g CaCO3/MgCO3 in 250 ml (33.3% HNO3)
- Gaseous CO₂ released measured using FT-IR
- Negligible CO₂ release (1.6% CaCO₃ / 0.0% MgCO₃) despite initial pH=1.2

Magnesium carbonate

Mineral carbonation

Diagram showing the process of mineral carbonation, including the flow of CO₂ from industrial processes to carbonation plants, the formation of (Ca, Mg) CO₃ for mineral reclamation, and the disposal or re-use of the product.
## Sources of metal oxide - Minerals

### Ultramafic igneous rocks containing large amounts of MgO

<table>
<thead>
<tr>
<th>Rock Type</th>
<th>MgO, wt%</th>
<th>CaO, wt%</th>
<th>RC</th>
<th>RCO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peridotites</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dunite</td>
<td>49.5</td>
<td>0.3</td>
<td>6.8</td>
<td>1.8</td>
</tr>
<tr>
<td>Harzburgite</td>
<td>45.4</td>
<td>0.7</td>
<td>7.3</td>
<td>2.0</td>
</tr>
<tr>
<td>Lherzolite</td>
<td>28.1</td>
<td>7.3</td>
<td>10.1</td>
<td>2.7</td>
</tr>
<tr>
<td>Serpentinite</td>
<td>~40</td>
<td>~0</td>
<td>~8.4</td>
<td>~2.3</td>
</tr>
<tr>
<td>Gabbro</td>
<td>~10</td>
<td>~13</td>
<td>~17</td>
<td>~4.7</td>
</tr>
<tr>
<td>Basalt</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Continental tholeiite</td>
<td>6.2</td>
<td>9.4</td>
<td>26</td>
<td>7.1</td>
</tr>
</tbody>
</table>
Sources of metal oxide - Minerals

Mg silicates are found in Ophiolite belt complexes

• US Klamath mountains: 3000 Gt

• A comprehensive evaluation of available minerals still missing

Olivine: \( \text{Mg}_2\text{SiO}_4 + 2\text{CO}_2 \leftrightarrow 2\text{MgCO}_3 + \text{SiO}_2 \)

Serpentine: \( \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 3\text{CO}_2 \leftrightarrow 3\text{MgCO}_3 + 2\text{SiO}_2 + 2\text{H}_2\text{O} \)

Wollastonite: \( \text{CaSiO}_3 + \text{CO}_2 \leftrightarrow \text{CaCO}_3 + \text{SiO}_2 \)
## Sources of metal oxide - Minerals

<table>
<thead>
<tr>
<th>MINERAL</th>
<th>FORMULA/COMPOSITION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basalt</td>
<td></td>
</tr>
<tr>
<td>Eclogite</td>
<td></td>
</tr>
<tr>
<td>Feldspar</td>
<td>CaAl$_2$Si$_2$O$_8$</td>
</tr>
<tr>
<td>Forsterite</td>
<td>Mg$_2$SiO$_4$</td>
</tr>
<tr>
<td>Glauconite$^a$</td>
<td>(K, Na, Ca)$<em>{1.2-2.0}$ (Fe$^{3+}$, Al, Fe$^{2+}$, Mg)$</em>{4.0}$</td>
</tr>
<tr>
<td></td>
<td>$x$ <a href="OH">Si$<em>{7.76}$Al$</em>{1.4}$O$_{20}$</a>$_4$ nH$_2$O</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>FeTiO$_3$</td>
</tr>
<tr>
<td>Listwanite</td>
<td>Carbonated serpentine</td>
</tr>
<tr>
<td>Magnetite</td>
<td>Fe$_3$O$_4$</td>
</tr>
<tr>
<td>Olivine</td>
<td>(Mg, Fe)$_2$SiO$_4$</td>
</tr>
<tr>
<td>Opoka$^a$</td>
<td>mainly CaCO$_3$, SiO$_2$, hematite and muscovite</td>
</tr>
<tr>
<td>Pyroxene</td>
<td>CaMgSi$_2$O$_6$ + (Fe, Al)</td>
</tr>
<tr>
<td>Serpentine$^f$</td>
<td>Mg$_3$Si$_2$O$_5$(OH)$_4$</td>
</tr>
<tr>
<td>Serpentinite</td>
<td></td>
</tr>
<tr>
<td>Talc</td>
<td>Mg$_3$Si$<em>4$O$</em>{10}$(OH)$_2$</td>
</tr>
<tr>
<td>Wollastonite</td>
<td>CaSiO$_3$</td>
</tr>
</tbody>
</table>
Sources of metal oxide - Residues

- **Steel Industry** (60-80 MtCO$_2$/y)
  - Steel slag
  - AOD process slag
  - Steel converter slag

- **Energy sector**
  - Lignite fly ash
  - APC fly ash
  - MSWI ash
  - PF ash

- **Cement industry**
  - Waste cement
  - Cement Kiln Dust

100s MtCO$_2$/y
Mineral carbonation – Process routes

• Gas-solid
  • Single-step
  • Multi-step

• Aqueous
  • Single-step
    • without chemicals
    • with chemicals
      • salts
      • bicarbonate
  • Multi-step (pH swing)
    • acid / base swing
    • P/T swing
    • chelant
Thermodynamics

\[ \Delta_r H = 400 \text{ kJ/mole} \]

Olivine

\[ \text{Mg}_2\text{SiO}_4 + 2 \text{CO}_2 \rightarrow \text{SiO}_2 + 2 \text{MgCO}_3 \]

\[ \Delta_r H = 90 \text{ kJ/mole} \]
**Gas-solid route**

- Thermodynamics favourable up to a maximum temperature
- Kinetics is very slow (geological times) at ambient temperature

Direct Gas-solid route

Chemistry of the process:

\[ x\text{MgO} \cdot y\text{SiO}_2 \cdot z\text{H}_2\text{O} \ (s) \]
\[ \Leftrightarrow x\text{MgO} \ (s) + y \text{ SiO}_2 \ (s) + z \text{ H}_2\text{O} \]  
(R1)

\[ \text{MgO} \ (s) + \text{CO}_2 \Leftrightarrow \text{MgCO}_3 \ (s). \]  
(R2)

- It can be applied only to pure Ca and Mg oxides and hydroxides
- Direct carbonation of silicates (R1+R2) is too slow
- Stepwise carbonation is required

Zevenhoven et al., Energy, 33 (2008)
Two-step Gas-solid route

- **Step 1:** production of free MgO / Mg(OH)$_2$
- **Step 2:** carbonation of MgO / Mg(OH)$_2$ to MgCO$_3$

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Zevenhoven et al., Energy, 33 (2008)
Two-step Gas-solid route

\[ \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4(s) \rightarrow 3\text{MgO}(s) + 2\text{SiO}_2(s) + 2\text{H}_2\text{O} \]

\[ \text{MgO}(s) + \text{H}_2\text{O} \leftrightarrow \text{Mg(OH)}_2(s) \]

\[ \text{Mg(OH)}_2(s) + \text{CO}_2 \leftrightarrow \text{MgCO}_3(s) + \text{H}_2\text{O} \]

**Route II: 3-steps carbonation**

Zevenhoven et al., Energy, 33 (2008)
Two-step Gas-solid route

Results of MgO and Mg(OH)$_2$ carbonation kinetics (74-125 μm)

Zevenhoven et al., GHGT-8 (2006)

<table>
<thead>
<tr>
<th>Year</th>
<th>Carbonation conditions</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>2002</td>
<td>1 355</td>
<td>MgO</td>
</tr>
<tr>
<td>2003</td>
<td>35 400</td>
<td>MgO</td>
</tr>
<tr>
<td>2004</td>
<td>35 510</td>
<td>Mg(OH)$_2$</td>
</tr>
<tr>
<td>2005</td>
<td>40 510</td>
<td>Mg(OH)$_2$</td>
</tr>
<tr>
<td>2006</td>
<td>40-45 525-540</td>
<td>Mg(OH)$_2$</td>
</tr>
</tbody>
</table>
**Aqueous route**

Aqueous carbonation consists of two processes: dissolution and precipitation

**Single-step**
- dissolution + precipitation (in a single reactor)

**Multi-step**
- dissolution
- precipitation

Two or more steps are needed when conditions of dissolution are too far from those required for precipitation to occur.
**Aqueous route**

\[
\text{CO}_2(\text{g}) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{HCO}_3^-(\text{aq}) \quad (1)
\]

\[
\text{Mg}_2\text{SiO}_4(s) + 4\text{H}^+(\text{aq}) \rightarrow 2\text{Mg}^{2+}(\text{aq}) + \text{SiO}_2(s) + 2\text{H}_2\text{O}(l) \quad (2)
\]

\[
\text{Mg}^{2+}(\text{aq}) + \text{HCO}_3^-(\text{aq}) \rightarrow \text{MgCO}_3(s) + \text{H}^+(\text{aq}) \quad (3)
\]

Bicarbonate/Salt mixture (NaHCO_3/NaCl) was proposed to accelerate the reaction: at these conditions (pH=7.7-8.0), reactions (2) and (3) are supposed to be replaced by:

\[
\text{Mg}_2\text{SiO}_4(s) + 2\text{HCO}_3^-(\text{aq}) \rightarrow 2\text{MgCO}_3(s) + \text{SiO}_2(s) + 2\text{OH}^-(\text{aq})
\]

\[
\text{OH}^-(\text{aq}) + \text{CO}_2(\text{g}) \rightarrow \text{HCO}_3^-(\text{aq})
\]
Aqueous route – Single step

Huijgen et al., Energy, Conversion and Mgmt (2006)
Seven regions with large ultramafic resources and large CO$_2$ point sources selected

Gerdemann et al., ES&T, 41 (2007)
Aqueous route – Single step

Samples ground to < 75μm heat treatment at 630°C for 2 hours

Gerdemann et al., ES&T, 41 (2007)
**Aqueous route – Single step**

### Optimum carbonation conditions

<table>
<thead>
<tr>
<th>Mineral</th>
<th>$T$, °C</th>
<th>$P_{\text{CO}_2}$, atm</th>
<th>Carrier solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>olivine</td>
<td>185</td>
<td>150</td>
<td>0.64 M NaHCO$_3$, 1 M NaCl</td>
</tr>
<tr>
<td>wollastonite</td>
<td>100</td>
<td>40</td>
<td>distilled water</td>
</tr>
<tr>
<td>HT serpentine</td>
<td>155</td>
<td>115</td>
<td>0.64 M NaHCO$_3$, 1 M NaCl</td>
</tr>
</tbody>
</table>

**$R_x$** = extent of reaction in 1h

**$R_x$(max) =** maximum extent of reaction in 1h

- olivine: 49.5%
- wollastonite: 81.8%
- HT serpentine: 73.5%

Aqueous route – Reactor design

Conventional Reactor
(Continuous Flow Leach-Type Autoclave)

Proposed Conceptual Reactor
(Pipe-Line Flow-Through Reactor)
Aqueous route – Mechanical activation

Mechanical activation of Olivine by milling

Influence on size distribution

Influence on specific area

Aqueous route – Mechanical activation

Dissolution kinetics of activated olivine

- Specific rate constant increases with milling time
- Activation is not correlated with the specific area

\[ r = -\frac{\partial[H^+]}{\partial t} = k[H^+] = \kappa(D \cdot S_{BET})[H^+] \]

<table>
<thead>
<tr>
<th>Product</th>
<th>( \kappa ) ([10^{-3} \text{ s}^{-1}])</th>
<th>( S_{BET} ) ([\text{m}^2/\text{g}])</th>
<th>( R^2 )</th>
<th>( D ) ([\text{g/l}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>AOX:1</td>
<td>0.9</td>
<td>1.18</td>
<td>0.998</td>
<td>10 and 20</td>
</tr>
<tr>
<td>AOX:5</td>
<td>1.5</td>
<td>3.44</td>
<td>0.959</td>
<td>5 and 10</td>
</tr>
<tr>
<td>AOX:15</td>
<td>2.3</td>
<td>3.88</td>
<td>1.000</td>
<td>2 and 5</td>
</tr>
<tr>
<td>AOX:30</td>
<td>4.7</td>
<td>2.99</td>
<td>0.985</td>
<td>1, 2 and 5</td>
</tr>
<tr>
<td>AOX:60</td>
<td>8.2</td>
<td>2.12</td>
<td>0.994</td>
<td>1 and 2</td>
</tr>
</tbody>
</table>
Aqueous route – Single step

S = silica
M = magnesite

Aqueous route – Single step

a: silica layer fracture and exfoliation

b: regrowth of new layer

Aqueous route – Single step

- Carbonation experiments at increased solid (forsterite) concentration
- Abrasion exposes fresh olivine reaction surface
- The silica-rich surface layer inhibites (passivates) carbonation

Aqueous route – Heat activation

- Thermal treatment of Lizardite (Serpentinite);
- Amorphous meta-serpentine is formed.

McKelvy et al., ES&T, 38 (2004)
Aqueous route – Heat activation

- No carbonation
- Trace carbonation
- Substantial carbonation

- Lizardite feedstock shows no reaction up to 185°C
- Material heated at 580°C showed trace reaction
- Materials heated at 610-720°C showed carbonation

McKelvy et al., ES&T, 38 (2004)
Aqueous carbonation – wollastonite

Huijgen et al., EST. 39 (2005)
Aqueous route – Single step

- Dissolution is the controlling mechanism
- Increase of dissolution rate can be achieved by:
  - physical/chemical mineral surface pre-treatment
  - increase of the specific area (grinding for size reduction)
  - removal of the silica passivating layer (abrasion / attrition)
  - addition of salts (NaCl/NaHCO₃)
- Dissolution experiments are needed to get process optimization
### Dissolution experiments - Serpentine

<table>
<thead>
<tr>
<th>Solvent ID</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>solvent#1</td>
<td>0.1M HCl</td>
</tr>
<tr>
<td>solvent#2</td>
<td>0.1 M Acetic Acid</td>
</tr>
<tr>
<td>solvent#3</td>
<td>0.1 M Acetic Acid + 0.1M Sodium Acetate</td>
</tr>
<tr>
<td>solvent#4</td>
<td>0.1M Acetic Acid + 0.1M Ascorbic Acid</td>
</tr>
<tr>
<td>solvent#5</td>
<td>0.1M Acetic Acid + 0.1M KHP</td>
</tr>
<tr>
<td>solvent#6</td>
<td>0.1M KH2PO4 + 0.1M CaCl2</td>
</tr>
<tr>
<td>solvent#7</td>
<td>1vol% Orthophosphoric Acid + 0.9wt% Oxalic Acid + 0.1wt% EDTA</td>
</tr>
<tr>
<td>solvent#8</td>
<td>0.1M Acetic Acid + 0.1wt% EDTA</td>
</tr>
<tr>
<td>solvent#9</td>
<td>0.1wt% EDTA</td>
</tr>
</tbody>
</table>

Dissolution experiments - Serpentine

- A fast dissolution phase is followed by a slow diffusion-limited one;

- Skeleton of $\text{SiO}_2$ or precipitation of iron oxide on the surface of serpentine particles hinders further dissolution of $\text{Mg}$

Dissolution experiments - Serpentine

Various methods of removing of SiO₂ layer

<table>
<thead>
<tr>
<th>Method</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal grinding (Glass beads)</td>
<td>Fluidization with 20 vol% of 2mm glass beads for 15 min (fluidizing gas = air, superficial gas velocity = 20 cm/s)</td>
</tr>
<tr>
<td>Internal grinding (Zirconia balls)</td>
<td>Fluidization with 20 vol% of 5mm zirconia balls for 15 min (fluidizing gas = air, superficial gas velocity = 7 cm/s)</td>
</tr>
</tbody>
</table>

Park and Fan, CES 59 (2004)
Dissolution experiments - Serpentine

- Internal grinding (20% beads) was not as effective as the external grinding (50% beads)
- Internal grinding was effective in refreshing the particles’ surface (aiding acid leaching)

No chemical additives (neutral pH)

Chemical additives (acidic pH)

Park and Fan, CES 59 (2004)
Dissolution experiments - Serpentine

- Serpentine from Cedar Hills quarry (SE Pennsylvania)
- Dissolution experiments on 50 g samples
- Three levels factors
- Sulphuric acid – Particle size – Reaction time

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Acid concentration (M)</th>
<th>Median particle size (μm)</th>
<th>Reaction time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.5</td>
<td>163</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>125</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>1.5</td>
<td>61</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>163</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>125</td>
<td>6</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>61</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
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<td>163</td>
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</tr>
<tr>
<td>8</td>
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</tr>
<tr>
<td>9</td>
<td>5</td>
<td>61</td>
<td>3</td>
</tr>
</tbody>
</table>

Alexander et al., Fuel, 86 (2007)
Dissolution experiments - Serpentine

- Particle size reduction: increase of surface area / increase of structural defects
- Protonation of the Mg-O-Si bonds facilitates removal of Mg atoms from the crystal lattice

Alexander et al., Fuel, 86 (2007)
Dissolution experiments - Serpentine

1. Loss of adsorbed water
2. Loss of crystallized water
3. Loss of OH groups

- Reduction of water content is correlated with Mg extraction.
- This demonstrates the significance of removing hydroxyl groups and the effectiveness of sulfuric acid in this removal.

Alexander et al., Fuel, 86 (2007)
Dissolution experiments - Serpentine

- Serpentine from a stockpile of the Hitura Ni mine (Outokumpu, Finland)
- Particle size fraction: 74-125um
- 1 g serpentine in 50 ml aqueous solution of 1,2, 4M solvents
- Temperature: 20°C – 1000 rpm stirring
- Acids for Mg leaching: HCl, H₂SO₄, HNO₃, HCOOH, CH₃COOH
- Base for Mg leaching: NaOH, KOH, NH₃, NH₄Cl, (NH₄)₂SO₄, NH₄NO₃

Dissolution experiments - Serpentine

- All solvents tested extracted a significant amount of Mg (3-26%) and Fe (2-16%)
- Extraction efficiency: $\text{H}_2\text{SO}_4 > \text{HCl} > \text{HNO}_3 > \text{HCOOH} > \text{CH}_3\text{COOH}$
- Low or no measurable amount of Mg extracted in NaOH, KOH, NH$_3$, NH$_4$Cl, (NH$_4$)$_2$SO$_4$, NH$_4$NO$_3$
- Slight influence of solvent concentration

$X =$ Extraction efficiency (measured at 1h, 20°C)

Dissolution experiments - Serpentine

- Faster dissolution measured at higher T
- Faster dissolution achieved with $\text{H}_2\text{SO}_4$

Dissolution experiments - Serpentine

- Faster Mg dissolution achieved with the finest size fraction
- Negligible Si dissolution (suggesting SiO₂ layer formation)

Conclusions:
- a successful carbonation process must also manage precipitation
- Recycling most of the additional chemicals used

Dissolution experiments - Olivine

- max. 200 bar / 200°C

Hänchen et al., CES, 62 (2007)
Dissolution model - Olivine

\[
\begin{align*}
\frac{dV}{dt} &= -Qc + R \\
\frac{dm}{dt} &= -R \\
R &= rkm^p
\end{align*}
\]

\[c(0) = c_o \text{ (initial solute conc.)} \]
\[m(0) = m_o \text{ (initial solid mass)} \]

- Mass balances for liquid and solid phases
- Dissolution rate proportional to surface area; no dependence on ion concentrations
- Total surface area proportional to \(m^p\), with \(p = 0.67\) for mono-sized convex particles with constant shape factors, and \(p > 0.67\) for particle size distributions. In the simulations \(p = 0.85\) was used for all experiments.
- Experimental data were fitted by choosing \(r\)
Dissolution experiments - Olivine

Slow dissolution (high pH)

- Model
- Experimental values
  - pH = 10.4
  - T = 90°C
  - Q = 10 ml/min
  - V = 170 ml
  - $r = 2.18 \times 10^{-13}$ mol/cm$^2$/s
  - $k = 6.15$ m$^2$/mol$^{0.85}$

Hänchen et al., CES, 62 (2007)
Dissolution experiments - Olivine

Fast dissolution (low pH)

- Model
- Experimental values
  - pH = 2
  - T = 120°C
  - V = 160 ml
  - Q = 10 ml/min
  - r = 1.03 \times 10^{-9} \text{ mol/cm}^2/\text{s}
  - k = 3.57 \text{ m}^2/\text{mol}^{0.85}

Hänchen et al., CES, 62 (2007)
Dissolution experiments - Olivine

\[ \log(r) = -n \text{pH} - \frac{E_A}{(RT)} + C \]

- **T = 150°C:**
  \[ \log(r) = -0.46 \text{pH} - 7.58 \]

- **T = 120°C:**
  \[ \log(r) = -0.46 \text{pH} - 8.07 \]

- **T = 90°C:**
  \[ \log(r) = -0.46 \text{pH} - 8.66 \]

- **T = 25°C:**
  \[ \log(r) = -0.50 \text{pH} - 10.64 \]

Activation energy:

\[ E_A = 52.9 \text{ kJ/mol} \]

25°C - Pokrovsky und Schott (2000)

• The pH change due to increasing CO2 pressure is similar to acid addition
• No evident effect of salt addition on dissolution rate (other than pH shift)

Precipitation experiments - Olivine

- Equilibrium Mg concentration at $T=120^\circ C$, $P(CO_2)=100$ atm
- Mg solubility strongly decrease at increasing Na ions concentration

Hänchen et al., CES, 62 (2007)
Precipitation experiments - Olivine

Supersaturation ratio

--- Hydromagnesite

__ Magnesite

T=120°C

P(CO₂)=100 bar

Hänchen et al., CES, 62 (2007)
Multi-step carbonation – HCl route

- The third step of the process has a positive Gibbs energy change
- HCl recover requires no formation of soluble chloride (no alkali metals)

Multi-step carbonation – pH swing

**Dissolution**
- 1% vol. Orthophosphoric acid
- 0.9% wt Oxalic acid
- 0.1% wt. EDTA
- internal grinding (2mm glass beads) – T= 70°C

**Product 1**
Undissolved solids
(rich in SiO₂ content)

**Precipitation**
- pH=8.6

**Product 2**
Iron oxide

**Precipitation**
- pH=9.5

**Product 3**
MgCO₃*3H₂O

NH₄OH  CO₂ (1 atm)

Park and Fan,
CES 59 (2004)
Multi-step carbonation – pH swing

• Preparation of Mg-rich solution from serpentine (Filtrate F2)
• HNO₃ and HCl selected for their low boiling points (83°C, 48-110°C)
• Mg carbonates precipitation at 30°C and CO₂ atmosphere of 1 atm
• Mg precipitation enhanced by NaOH addition (pH swing)

Multi-step carbonation – pH swing

- Mg-rich solution from HNO$_3$ enhanced serpentine dissolution
- Increasing pH values obtained by adding increasing NaOH (50 %wt)
- Hydromagnesite (hydrated Mg carbonate) was formed
- Highest Mg conversion at pH=9 (0.9-1.2 g NaOH/g hydromagnesite)

Multi-step carbonation – pH swing

- Mg-rich solution from HCl enhanced serpentine dissolution
- Increasing pH values obtained by adding increasing NaOH (50 %wt)
- Hydromagnesite and Magnesite were formed
- Highest Mg conversion at pH=9 (0.9-1.2 g NaOH/g hydromagnesite)

Multi-step carbonation – pH swing

Mass balance of elements

Process cost
- HCl: 1300 USD/t CO₂
- HNO₃: 1600 USD/t CO₂

Multi-step carbonation – Acetic acid route

- Dissolution of wollastonite and CaCO₃ precipitation
- Acetic acid pKa (4.76) is between pKa of Carbonic (3.6) and Silicic acid (9.51)
- This allows the acid to be replaced by carbonic acid in the crystallization step

Kakizawa et al., Energy, 26 (2001)
Multi-step carbonation – Acetic acid route

- Dissolution performed at $T=60^\circ C$ (L/S = 5/1, 300 rpm)
- Acetic acid/ Water = 13.72 g / 50 g
- Decrease of dissolution rate with time ascribed to $\text{SiO}_2$ deposition

Kakizawa et al., Energy, 26 (2001)
Multi-step carbonation – Acetic acid route

- Precipitation performed at T=40-80°C from calcium acetate solutions
- Magnetic stirring (0-300 rpm) – P(CO₂)=5-50 bar

Kakizawa et al., Energy, 26 (2001)
Multi-step carbonation – Acetic acid route

Energy requirements

100 MW oil fired thermal power plant (40% efficiency)

Stirred tank reactor for dissolution: 60°C, 300 rpm, T=60 min, 20um particles

Crystallization process: 60°C, P(CO₂)=30 bar, 100 rpm, T=10min,

<table>
<thead>
<tr>
<th>Break-down of the energy consumption for the disposal process</th>
<th>Energy consumption [MW]</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ separation</td>
<td>5.56</td>
<td>27.28</td>
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<tr>
<td>CO₂ compression</td>
<td>4.65</td>
<td>22.82</td>
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<tr>
<td>Pulverization</td>
<td>5.29</td>
<td>25.96</td>
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<tr>
<td>Extraction</td>
<td>1.27</td>
<td>6.23</td>
</tr>
<tr>
<td>Crystallization</td>
<td>2.60</td>
<td>12.76</td>
</tr>
<tr>
<td>CaCO₃ separation</td>
<td>1.01</td>
<td>4.96</td>
</tr>
<tr>
<td>Total</td>
<td>20.38</td>
<td>100</td>
</tr>
</tbody>
</table>

20% energy penalty

Kakizawa et al., Energy, 26 (2001)
Patents on mineral carbonation

- Toulhoat et al., (IFP, F) 2005 (EP)
- Geerlings et al., (Shell, NL) 2007 (WO, US)
- Gorset et al., (Institut for Energiteknikk, NO) 2007 (WO)
- Park and Fan (Dinsmore & Shohl LLP, US) 2005 (US)
- Maroto-Valer et al., (Penn State Research Fundation, US) 2004 (WO), 2005 (US)
- Blencoe et al., (Battelle, US) 2004 (WO), 2008 (US)
Patents on mineral carbonation

Toulhoat et al., (IFP, F) 2005 (EP)

- Aqueous mineral carbonation / Multi step process
- Step 1: CO₂ concentration in liquid phase
  a) CO₂ liquefaction: a liquid CO₂ stream is obtained
  b) absorption of CO₂: polar liquid, ionic liquid, amine, liquid with enzymes: a CO₂ solution in an aprotic polar liquid is obtained
- Step 2: Electro-reduction in an aprotic liquid
  pH=3-5, Anode V= 0.5-3.5 V(H₂)
- Step 3: Back extraction of oxalic/formic acid into the aqueous phase (optional, if step 2 was made in a non-aqueous phase)
- Step 4: Mineralization by reaction of a metal (M=Ca,Mg) carbonate with the acid:

\[
\begin{align*}
\text{MCO}_3 + (\text{COOH})_2 & \rightarrow \text{MC}_2\text{O}_4 + \text{CO}_2 + \text{H}_2\text{O} \quad \text{or} \\
\text{MCO}_3 + 2 \text{HCOOH} & \rightarrow \text{M(HCO}_2\text{)}_2 + \text{CO}_2 + \text{H}_2\text{O}
\end{align*}
\]
Patents on mineral carbonation


- Aqueous mineral carbonation / Single step process
- Materials: orthosilicates, disilicates, cyclosilicates (forsterite, olivine, wollastonite, monticellite, diposide, enstatite) – phyllosilicates (sheet) /tectosilicates not suitable
- Maximum average size: 200 μm (but > 10 μm) to avoid excessive energy for grinding
- Electrolyte aqueous solution (NaCl, KCl, BaCl₂, NaNO₃, KNO₃, Ba(NO₃)₂) 0.1-2.0 M
- Temperature: 100-200 °C
- CO₂ pressure: 1-50 bar a; Total pressure: 1-150 bar a
- Reactor: Slurry bubble column / Extruder (just mentioned – no design given)
- Product use: construction materials: building blocks, paving stones, roofing tiles

CaO production (carbon neutral)
Patents on mineral carbonation

Geerlings et al., (Shell, NL) 2007 (WO,US)

- The patent applies to sheet silicates (serpentine, talc) excluded from previous patent
- The patent claims that hot synthesis gas is typically available where CO₂ is produced
- Sheet silicates are converted to ortho- or chain- silicates by thermal activation
- Thermal activation obtained by direct heating with hot synthesis gas
- Conversion Temperature: 600-800°C (serpentine to amorphous olivine Mg₂SiO₄)
  800-1000°C (talc to enstatite MgSiO₃)
- Contact reactor: fluidized bed of silicate hydroxide particles
- Water produced in the thermal activation may be used in the water gas-shift reaction
- Activated silica is then contacted with CO₂ in a slurry reactor (aqueous carbonation)
- Mineral carbonation T and P as per previous Shell patent
Patents on mineral carbonation

Geerlings et al., (Shell, NL) 2007 (WO,US)

Synthesys Gas
Coal Gasification
CO: 65% mol
H2: 25%
N2: 5%
CO2: 1.5%
H2O: 2.5%

Heat treatment
100 kmol
1500 °C

Water Gas-shift
600 °C
100 kmol
36.5 kmol CO₂
1604 kg CO₂

Q = 3165 MJ
(2394 kg serpentine converted to olivine)

1192 kg CO₂
Sequestered (71% of CO₂ produced)
Patents on mineral carbonation

Gorset et al., (Institut for Energiteknikk, NO) 2007 (WO)

- The patent applies to olivine (forsterite)
- Aqueous mineral carbonation / multi-step
- Pressure/Temperature swing
- No chemicals addition
- R1 – Dissolution
  pH=3-5 P=50-150 bar / T= 100-170°C
- R2 – MgCO₃ precipitation
  pH >> P= 50-80 bar / T= 140-250 °C
- R3 – SiO₂ precipitation
  T lower than in step R2
Patents on mineral carbonation

Gorset et al., (Institut for Energiteknikk, NO) 2007 (WO)

- Dissolution in test packed bed reactor: \( T=130^\circ C \), \( P=150 \text{ bar} \)
  flow 0.71 ml/min water + 0.04 ml/min \( CO_2 \)

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Pre-preparation</th>
<th>Weight before</th>
<th>BET before</th>
<th>Weight loss</th>
<th>Weight loss</th>
<th>Duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olivine 11</td>
<td>Planetary mill, 10 min, dry</td>
<td>0.49</td>
<td>4.32</td>
<td>0.34</td>
<td>70</td>
<td>45</td>
</tr>
<tr>
<td>Olivine 12</td>
<td>Planetary mill, 60 min, dry</td>
<td>0.48</td>
<td>3.19</td>
<td>0.32</td>
<td>67</td>
<td>28</td>
</tr>
<tr>
<td>Olivine 14</td>
<td>sieved, 75-150 ( \mu m )</td>
<td>1.14</td>
<td>0.87</td>
<td>1.12</td>
<td>98</td>
<td>76</td>
</tr>
</tbody>
</table>

- Precipitation reactor: \( T=250^\circ C \), \( P=150 \text{ bar} \); no-mix

![Diagram of the dissolution tests](Image)

![Diagram of the precipitation reactor](Image)

![Table 2: Mineral chemistry of precipitated magnesite](Image)
**Patents on mineral carbonation**

**Park and Fan (Dinsmore & Shohl LLP, US) 2005 (US)**

- Aqueous phase / Multi-step
- pH swing
- Material: serpentine
- Slurry fluidized bed reactor
- Particle size: 100-500 um
- Step 1: dissolution with weak acid
- Step 2: precipitation of iron oxide
- Step 3: precipitation of MgCO3

- Conditions same as in the literature
Multi-step carbonation – pH swing

Dissolution
- 1% vol. Orthophosphoric acid
- 0.9% wt Oxalic acid
- 0.1% wt. EDTA
- internal grinding (2mm glass beads) – $T= 70^\circ C$

Product 1
Undissolved solids
(rich in SiO$_2$ content)

Mg- and Fe- rich solution

Precipitation
pH=8.6

Product 2
Iron oxide

Precipitation
pH=9.5

Product 3
MgCO$_3$*3H$_2$O

$\text{NH}_4\text{OH}$ $\text{CO}_2$ (1 atm)

Park and Fan, CES 59 (2004)
Patents on mineral carbonation

Blencoe et al., (Battelle, US) 2004 (WO), 2008 (US)

• Aqueous mineral carbonation / Multi step process
• Materials: calcium silicates: wollastonite, calcic plagioclase, waste concrete; magnesium silicates: olivine (forsterite), serpentine, basalt.
• Average particle size: 100 um is preferred.
• Step 1: Reaction of a silicate with NaOH (30-80% wt.in water) to form an hydroxide of the metal formerly in the silicate, which is segregated
• step 2: Reaction of carbon dioxide (flue gas) with either NaOH or Na$_2$SiO$_3$ to form Na$_2$CO$_3$ or NaHCO$_3$.
• Step 3: the metal hydroxide (step 1) is reacted with the carbonate/bicarbonate (step 2) to produce a carbonate of the metal formerly in the silicate. The caustic material produced here can be recycled to step 1.
• Pressure: slightly below vapor pressure of water (Step 1)
• Pressure: 10-30 bar above vapor pressure of water at the operating T (Steps 2/3)
Patents on mineral carbonation

Blencoe et al., (Battelle, US) 2004 (WO), 2008 (US)

Wollastonite

- **Step 1**  \[ \text{CaSiO}_3 + \text{NaOH(aq)} \rightarrow \text{NaCaSiO}_3(\text{OH})(\downarrow), \]  
  wollastonite      sodium-calcium hydroxysilicate

- **Step 2**  \[ 2\text{NaOH(aq)} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O(liq)} \]

- **Step 3**  \[ \text{Na}_2\text{CO}_3(\text{aq}) + 3\text{NaCaSiO}_3(\text{OH}) + \text{H}_2\text{O} \rightarrow \]  
  \[ 4\text{NaOH(aq)} + \text{CaCO}_3(\downarrow) + \text{NaCa}_2\text{Si}_3\text{O}_8(\text{OH})(\downarrow) \]  
  calcite      pectolite
Patents on mineral carbonation

Blencoe et al., (Battelle, US) 2004 (WO), 2008 (US)

Anorthite

- **Step 1** \(3 \text{CaAl}_2\text{Si}_2\text{O}_8 + 8\text{NaOH(aq)} \rightarrow 3\text{Ca(OH)}_2(\downarrow) + \text{Na}_8(\text{AlSiO}_4)_6(\text{OH})_2(\downarrow),\)  
  anorthite \hspace{1cm} \text{portlandite} \hspace{1cm} \text{hydroxy-sodalite}

- **Step 2** \(2\text{NaOH(aq)} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O(liq)}\)

- **Step 3** \(2\text{Na}_2\text{CO}_3(\text{aq}) + \text{Ca(OH)}_2 + \text{Na}_8(\text{AlSiO}_4)_6(\text{OH})_2 + 2\text{H}_2\text{O(liq)} \rightarrow \)

  \[4\text{NaOH(aq)} + \text{CaCO}_3(\downarrow) + \text{Na}_8(\text{AlSiO}_4)_6\text{CO}_3 \cdot 2\text{H}_2\text{O(\downarrow)}.\]  
  calcite \hspace{1cm} \text{carbonate-cancrinite}
## Patents on mineral carbonation

Blencoe et al., (Battelle, US) 2004 (WO), 2008 (US)

<table>
<thead>
<tr>
<th>Date/Duration@</th>
<th>Starting Materials@,#</th>
<th>Temperature/Pressure</th>
<th>XRD Number</th>
<th>Solid Run Products, and Initial/Final Solution pH%</th>
</tr>
</thead>
<tbody>
<tr>
<td>7-10-02/72 hrs</td>
<td>anorthite + NaOH + H₂O</td>
<td>200°C/ &lt;15 atm</td>
<td>LMAS001-2</td>
<td>portlandite + hydroxy-sodalite + hydrosodalite(?)</td>
</tr>
<tr>
<td>8-1-02/72 hrs</td>
<td>anorthite + NaOH + Na₂CO₃ + H₂O</td>
<td>200°C/ &lt;15 atm</td>
<td>LMA059</td>
<td>calcite + hydroxy-sodalite</td>
</tr>
<tr>
<td>10-4-02/72 hrs</td>
<td>prereacted anorthite + Na₂CO₃ + H₂O</td>
<td>200°C/ &lt;15 atm</td>
<td>LMA070</td>
<td>calcite + carbonate-cancrinite, pH: 12.5/≥14</td>
</tr>
<tr>
<td>11-26-02/72 hrs</td>
<td>wollastonite + NaOH + H₂O</td>
<td>200°C/ &lt;15 atm</td>
<td>LMA081</td>
<td>sodium-calcium hydroxysilicate</td>
</tr>
<tr>
<td>12-2-02/72 hrs</td>
<td>wollastonite + NaOH + Na₂CO₃ + H₂O</td>
<td>200°C/ &lt;15 atm</td>
<td>LMA083</td>
<td>calcite + sodium-calcium hydroxysilicate, pH: 12.5/≥14</td>
</tr>
<tr>
<td>12-17-02/72 hrs</td>
<td>Ca(OH)₂ + Na₂CO₃ + H₂O</td>
<td>200°C/ &lt;15 atm</td>
<td>LMA089</td>
<td>calcite, pH: 12.5/≥14</td>
</tr>
</tbody>
</table>
Patents on mineral carbonation

Blencoe et al., (Battelle, US) 2004 (WO), 2008 (US)

Olivine

- Step 1  \[ \text{Mg}_2\text{SiO}_4 + 2\text{NaOH(aq)} + \text{H}_2\text{O(liq)} \rightarrow 2\text{Mg(OH)}_2(\downarrow) + \text{Na}_2\text{SiO}_3(aq) \]

  olivine  \hspace{1cm} \text{brucite}

- Step 2  \[ \text{Na}_2\text{SiO}_3(aq) + 2\text{CO}_2 + \text{H}_2\text{O(liq)} \rightarrow 2\text{NaHCO}_3(aq) + \text{SiO}_2(\downarrow) \]

- Step 3  \[ 2\text{Mg(OH)}_2 + 2\text{NaHCO}_3(aq) \rightarrow 2\text{MgCO}_3(\downarrow) + 2\text{NaOH(aq)} + 2\text{H}_2\text{O(liq)} \]

  brucite  \hspace{1cm} \text{magnesite}
**Patents on mineral carbonation**

Blencoe et al., (Battelle, US) 2004 (WO), 2008 (US)

**Serpentine**

- **Step 1** $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{NaOH}(\text{aq}) \rightarrow 3\text{Mg(OH)}_2(\downarrow) + \text{Na}_2\text{SiO}_3(\text{aq}) + \text{SiO}_2$
  - serpentine
  - brucite

- **Step 2** $\text{Na}_2\text{SiO}_3(\text{aq}) + 2\text{CO}_2 + \text{H}_2\text{O}(\text{liq}) \rightarrow 2\text{NaHCO}_3(\text{aq}) + \text{SiO}_2(\downarrow)$

- **Step 3** $2\text{Mg(OH)}_2 + 2\text{NaHCO}_3(\text{aq}) \rightarrow 2\text{MgCO}_3(\downarrow) + 2\text{NaOH}(\text{aq}) + 2\text{H}_2\text{O}(\text{liq})$
  - brucite
  - magnesite

  $\text{Mg(OH)}_2 + \text{CO}_2 \rightarrow \text{MgCO}_3(\downarrow) + \text{H}_2\text{O}(\text{liq})$
  - brucite
  - magnesite
## Patents on mineral carbonation

**Blencoe et al., (Battelle, US) 2004 (WO), 2008 (US)**

<table>
<thead>
<tr>
<th>Date/Duration</th>
<th>Starting Materials</th>
<th>Temperature/Pressure</th>
<th>XRD Number</th>
<th>Solid Run Products, and Initial/Final Solution pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-10-02/72 hrs</td>
<td>serpentine + NaOH + H₂O</td>
<td>200°C/ &lt;15 atm</td>
<td>LMAS001-1</td>
<td>brucite + relict serpentine</td>
</tr>
<tr>
<td>7-1-02/72 hrs</td>
<td>olivine + NaOH + H₂O</td>
<td>200°C/ &lt;15 atm</td>
<td>-</td>
<td>brucite</td>
</tr>
<tr>
<td>7-16-02/72 hrs</td>
<td>prereacted olivine + Na₂CO₃ + H₂O</td>
<td>200°C/ &lt;15 atm</td>
<td>LMAS006</td>
<td>brucite</td>
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<td>9-20-02/24 hrs</td>
<td>serpentine + NaOH + H₂O</td>
<td>200°C/ &lt;15 atm</td>
<td>LMA069</td>
<td>brucite + trace AUCP</td>
</tr>
<tr>
<td>9-23-02/72 hrs</td>
<td>serpentine + NaOH + H₂O</td>
<td>200°C/ &lt;15 atm</td>
<td>LMA067</td>
<td>brucite + trace AUCP</td>
</tr>
<tr>
<td>9-25-02/72 hrs</td>
<td>Mg(OH)₂ + Na₂CO₃ + H₂O</td>
<td>200°C/ &lt;15 atm</td>
<td>LMA072</td>
<td>brucite, pH: 12.5/12.5</td>
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<tr>
<td>10-17-02/72 hrs</td>
<td>serpentine + NaOH + H₂O</td>
<td>22°C/ 1 atm</td>
<td>LMA073</td>
<td>serpentine + brucite</td>
</tr>
<tr>
<td>10-18-02/72 hrs at 22°C, then 3 hrs at 200°C</td>
<td>serpentine + NaOH + H₂O</td>
<td>22°C/ 1 atm, 200°C/ &lt;15 atm</td>
<td>LMA075</td>
<td>brucite + minor relict serpentine</td>
</tr>
</tbody>
</table>
## Patents on mineral carbonation

Blencoe et al., (Battelle, US) 2004 (WO), 2008 (US)

<table>
<thead>
<tr>
<th>Date/Duration</th>
<th>Starting Materials</th>
<th>Temperature/Pressure</th>
<th>XRD Number</th>
<th>Solid Run Products, and Initial/Final Solution pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-21-03/72 hrs</td>
<td>Mg(OH)$_2$ + Na$_2$CO$_3$ + H$_2$O</td>
<td>80°C/ &lt;1 atm</td>
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<td>brucite + magnesium carbonate hydrate, pH: 12.5/12.5</td>
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<td>4-07-03/72 hrs</td>
<td>Mg(OH)$_2$ + Na$_2$CO$_3$ + H$_2$O</td>
<td>125°C/ &lt;2 atm</td>
<td>LMAS030</td>
<td>brucite + magnesium carbonate hydrate, final pH: 11.5</td>
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<tr>
<td>4-16-03/72 hrs</td>
<td>Mg(OH)$_2$ + NaHCO$_3$ + H$_2$O</td>
<td>200°C/ &lt;15 atm</td>
<td></td>
<td>magnesite + minor eitelite + minor relict brucite</td>
</tr>
<tr>
<td>11-15-02/72 hrs</td>
<td>Mg(OH)$_2$ + Na$_2$CO$_3$ + H$_2$O</td>
<td>300°C/ &lt;86 atm</td>
<td>LMA078</td>
<td>brucite</td>
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<tr>
<td>11-19-02/1 hr</td>
<td>Mg(OH)$_2$ + Na$_2$CO$_3$ + H$_2$O</td>
<td>375°C/ &lt;220 atm</td>
<td>LMA079</td>
<td>brucite</td>
</tr>
<tr>
<td>12-23-02/72 hrs</td>
<td>Mg(OH)$_2$ + Na$_2$CO$_3$ + H$_2$O</td>
<td>200°C/ &lt;60 atm</td>
<td>LMA088</td>
<td>eitelite + minor relict brucite</td>
</tr>
<tr>
<td>12-30-02/72 hrs</td>
<td>Mg(OH)$_2$ + H$_2$O</td>
<td>200°C/ &lt;60 atm</td>
<td>LMA090</td>
<td>magnesite + minor relict brucite, final pH: 5.5</td>
</tr>
<tr>
<td>1-17-03/72 hrs</td>
<td>Mg(OH)$_2$ + Na$_2$CO$_3$ + H$_2$O</td>
<td>300°C/ &lt;60 atm</td>
<td>LMAS014</td>
<td>brucite + eitelite, pH: 11.5-12/12</td>
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<tr>
<td>3-17-03/72 hrs</td>
<td>Mg(OH)$_2$ + Na$_2$CO$_3$ + H$_2$O</td>
<td>100°C/ &lt;1 atm</td>
<td>LMAS017</td>
<td>brucite + magnesium carbonate hydrate</td>
</tr>
</tbody>
</table>
Patents on mineral carbonation

Maroto-Valer et al., (Penn State Research Fundation, US) 2004 (WO), 2005 (US)

- Aqueous mineral carbonation / Two step process
- Materials: silicate-based Ca/Mg minerals or materials (olivine, serpentine, waste cement)
- Particle size: 70-150 μm
- Step 1: chemical activation with an acid: T=15 - 75°C; 3-12 hours time
  \[ \text{Mg}_3\text{Si}_2\text{O}_5\text{(OH)}_4 + 3 \text{H}_2\text{SO}_4 \rightarrow 3 \text{MgSO}_4 + 5 \text{H}_2\text{O} + 2 \text{SiO}_2 \]
- Step 2a: Use of a base (KOH, NaOH, NaHCO\textsubscript{3}, Acetates, Formates (pH=7-14)
  \[ \text{MgSO}_4 + 2 \text{NaOH} \rightarrow \text{Mg(OH)}_2 + \text{Na}_2\text{SO}_4 \]
- Step 2b: addition of Ca(NO\textsubscript{3})\textsubscript{2}
  \[ \text{MgSO}_4 + \text{Ca(NO}_3)_2 + 2 \text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{Mg(NO}_3)_2 \]
  \[ \text{Mg(NO}_3)_2 + \text{Ca(OH)}_2 \rightarrow \text{Mg(OH)}_2 + \text{Ca(NO}_3)_2 \]
- Step 3: Mg carbonate precipitation and acid recovery (reaction with CO\textsubscript{2})
  \[ \text{Mg(OH)}_2 + \text{CO}_2 \rightarrow \text{MgCO}_3 + \text{H}_2\text{O} \]
  \[ \text{MgSO}_4 + \text{H}_2\text{CO}_3 \rightarrow \text{MgCO}_3 + \text{H}_2\text{SO}_4 \]
**Patents on mineral carbonation**

Maroto-Valer et al., (Penn State Research Fundation, US) 2004 (WO), 2005 (US)

- **Step 1:** dissolution of the mineral

<table>
<thead>
<tr>
<th>Treatment</th>
<th>% Mg$^{2+}$ in solution</th>
<th>Activation Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfuric Acid</td>
<td>71</td>
<td>25°C, 12 hours</td>
</tr>
<tr>
<td>Hydrochloric Acid</td>
<td>21</td>
<td>25°C, 12 hours</td>
</tr>
<tr>
<td>Phosphoric Acid</td>
<td>25</td>
<td>25°C, 12 hours</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>48*</td>
<td>60°C, 4 hours*</td>
</tr>
</tbody>
</table>

* Maximum extraction yield reported in the literature using acetic acid (Kakizawa et al., 2001).

- **Step 2:** conversion of Mg(OH)$_2$/MgSO$_4$ to MgCO$_3$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conversion</th>
<th>Carbonation Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parent, untreated</td>
<td>8 %</td>
<td>155°C, 1850 psig, 1 hour</td>
</tr>
<tr>
<td>Steam treated</td>
<td>70%</td>
<td>155°C, 1850 psig, 1 hour</td>
</tr>
<tr>
<td>Mg(OH)$_2$</td>
<td>&gt;55%</td>
<td>20°C, 650 psig, 3 hours</td>
</tr>
<tr>
<td>MgSO$_4$</td>
<td>54%</td>
<td>20°C, 650 psig, 6 hours</td>
</tr>
<tr>
<td>Mg Acetate</td>
<td>30%</td>
<td>20°C, 650 psig, 3 hours</td>
</tr>
</tbody>
</table>
Carbonation of residues

- Industrial residues are often associated with CO$_2$ point source emissions
- They also tend to be more unstable than geologically derived materials
- They require a lower degree of pre-treatment and less energy intensive conditions
- Carbonation may also be seen as a stabilisation process
- The leaching behaviour of alkaline residues may be improved by stabilisation

<table>
<thead>
<tr>
<th>Sample</th>
<th>CaO</th>
<th>SiO$_2$</th>
<th>MgO</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>65.04</td>
<td>20.71</td>
<td>1.03</td>
<td>4.83</td>
<td>2.77</td>
</tr>
<tr>
<td>PFA</td>
<td>3.36</td>
<td>46.96</td>
<td>1.76</td>
<td>23.71</td>
<td>11.33</td>
</tr>
<tr>
<td>GGBS</td>
<td>41.38</td>
<td>34.59</td>
<td>6.84</td>
<td>14.02</td>
<td>1.51</td>
</tr>
<tr>
<td>MSWI-b</td>
<td>22.62</td>
<td>10.32</td>
<td>1.61</td>
<td>5.30</td>
<td>0.95</td>
</tr>
<tr>
<td>MSWI-f</td>
<td>35.89</td>
<td>15.29</td>
<td>1.29</td>
<td>6.25</td>
<td>1.11</td>
</tr>
<tr>
<td>Deinking Ash</td>
<td>37.69</td>
<td>33.76</td>
<td>3.72</td>
<td>20.12</td>
<td>0.03</td>
</tr>
<tr>
<td>Stainless Steel Slag</td>
<td>46.66</td>
<td>27.92</td>
<td>9.75</td>
<td>2.91</td>
<td>1.22</td>
</tr>
</tbody>
</table>

OPC: Ordinary portland cement  
PFA: Pulverized fly ash (coal fired power station)  
GGBS: Ground granulated Blast Furnace Slags  
MSWI-b: Municipal Solid Waste Incineration (Bottom ash)  
MSWI-f: Municipal Solid Waste Incineration (Fly ash)
Carbonation of residues – steel slags

- Aqueous phase / Single step
- Material: stainless steel slags
- pH=12.6
- Slurry reactor
- No chemicals addition
- Different size fractions tested
- T= 20-225°C
- P= 1-30 bar (Pure CO₂)
- Max CO₂ capacity: 0.25 kgCO₂/kg slag

Huijgen et al., EST. 39 (2005)
Carbonation of residues – steel slags

Huijgen et al., EST. 39 (2005)
Carbonation of residues – steel slags

Optimal operating conditions:

- \( P = 20 \text{ bar} \)
- \( T = 200^\circ\text{C} \); \( \text{L/S} = 5 \) (lower is better)
- \( d < 106 \, \mu\text{m} \) (38 \( \mu\text{m} \) preferred)

\[
\eta_{\text{CO}_2}[\%] = \frac{\text{CO}_2_{\text{avoided}}}{\text{CO}_2_{\text{sequestered}}} \times 100 = \\
100 - \frac{E_{\text{power}}/E_{\text{power}} + E_{\text{heat}}/E_{\text{heat}}}{\text{CO}_2_{\text{sequestered}}} \times 100 \tag{2}
\]

Carbonation of residues – steel slags

Fresh sample

Carbonated sample

- Carbonation takes place in two steps: dissolution and precipitation
- Ca diffusion to the surface controlling mechanism
- A carbonate coating forms on the particles
- A SiO2 rim is also observed (XRD)
- This hinders Ca diffusion to the particle surface
- pH reduction related to carbonation extent

Huijgen et al., EST. 39 (2005)
Carbonation of residues – Waste cement

- Waste cement is a Ca rich waste
- Produced in the process for aggregates recovery from concrete
- Reuse of waste cement limited to use as roadbed material
- A long term waste cement supply from building demolition expected
- Carbonation is expected to follow this reaction scheme (dissolution and precipitation):

\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{CO}_3 \quad (1) \\
\text{H}_2\text{CO}_3 & \rightarrow \text{H}^+ + \text{HCO}_3^- \quad (2) \\
\text{HCO}_3^- & \rightarrow \text{H}^+ + \text{CO}_3^{2-} \quad (3)
\end{align*}
\]

\[
\begin{align*}
3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} + 6\text{H}^+ & \rightarrow 3\text{Ca}^{2+} + 2\text{SiO}_2 + 6\text{H}_2\text{O} \quad (4) \\
\text{Ca(OH)}_2 + 2\text{H}^+ & \rightarrow \text{Ca}^{2+} + 2\text{H}_2\text{O} \quad (5) \\
\text{Ca}^{2+} + \text{CO}_3^{2-} & \rightarrow \text{CaCO}_3 \downarrow \quad (6)
\end{align*}
\]

Carbonation of residues – Waste cement

- Waste cement
- Particle size: 10-200 μm
- Ca content: 27%
- 11% Ca bound as carbonate
- CO₂ storage capacity: 0.27 t/t

- Calcium extraction tests
- Batch vessel: 500 ml volume
- Operating parameters:
  - Pressure
  - L/S ratio
  - T=323 K (50°C)

Carbonation of residues – Waste cement

Calcium extraction rate at the initial stage of the reaction (3 minutes)

### Carbonation of residues – Waste cement

![Graphs showing calcium utilization ratio and energy consumption for different pressures and waste cement ratios.](image)

<table>
<thead>
<tr>
<th></th>
<th>CO₂ separation</th>
<th>pressurization</th>
<th>stirring</th>
<th>pulverization</th>
<th>revenue by selling CaCO₃</th>
<th>total</th>
</tr>
</thead>
<tbody>
<tr>
<td>power consumption per 100 MW of power generation (MW/100 MW)</td>
<td>5.5</td>
<td>13.7</td>
<td>0.32</td>
<td>6.4</td>
<td>25.9</td>
<td></td>
</tr>
<tr>
<td>power consumption for CO₂ treatment [(kW h)/t of CO₂]</td>
<td>89</td>
<td>223</td>
<td>5</td>
<td>104</td>
<td>421</td>
<td></td>
</tr>
<tr>
<td>operating cost for CO₂ treatment [$/t of CO₂]</td>
<td>7.9</td>
<td>19.9</td>
<td>0.55</td>
<td>9.3</td>
<td>22.6</td>
<td></td>
</tr>
</tbody>
</table>

*The ratio of the calcium in the waste cement utilized for the CO₂ treatment is 18.1%.*
Carbonation of residues – CKD

<table>
<thead>
<tr>
<th>CKD Type</th>
<th>Kiln Type</th>
<th>Collection System</th>
</tr>
</thead>
<tbody>
<tr>
<td>AG Bypass High¹</td>
<td>Dry</td>
<td>Alkali Bypass System</td>
</tr>
<tr>
<td>AG Bypass Low¹</td>
<td>Dry</td>
<td>Alkali Bypass System</td>
</tr>
<tr>
<td>AG Wet²</td>
<td>Wet</td>
<td>Baghouse/Electrostatic Precipitator</td>
</tr>
<tr>
<td>Continental Wet³</td>
<td>Wet</td>
<td>Baghouse/Electrostatic Precipitator</td>
</tr>
</tbody>
</table>

Cement industry: \(0.81 \text{ tCO}_2/\text{t cement}\)

Cement industry

- World cement production:
- Emissions: 0.7-0.8 \(\text{tCO}_2/\text{t cement}\)
- CKD=0.1-0.2 t/t cement
  (20-30 kg/t cement sent to landfill)
- CKD potential hazardous waste
- Leaching of heavy metals
- CKD recycle already made (need to remove alkali compounds)
Carbonation of residues – CKD

- Wet carbonation
- $T=25^\circ C$
- $PCO_2 = 1$ bar
- 100% RH
- $L/S = 0.85$

\[
\xi(t) = \frac{M_{CO_2}(t)}{M(t=0) \cdot ThCO_2}
\]
Carbonation of residues – CKD

- Wet carbonation
- T=25°C
- PCO₂ = 1 bar
- 100% RH
- L/S variable

\[ \xi(t) = \frac{M_{CO_2}(t)}{M(t = 0) \cdot ThCO_2} \]
Carbonation of residues – CKD

Cement Kiln Dust

<table>
<thead>
<tr>
<th>CKD Type</th>
<th>w/s</th>
<th>Reaction Time (days)</th>
<th>Relative Humidity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AG Bypass High</td>
<td>0.00</td>
<td>0.3, 1, 2, 4, 6, 8</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.00, 0.06, 0.25, 0.4, 0.85, 1.15</td>
<td>2</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.85</td>
<td>0.3, 1, 2, 4, 6, 8</td>
<td>100</td>
</tr>
<tr>
<td>AG Bypass Low</td>
<td>0.00</td>
<td>0.3, 1, 2, 4, 6, 8</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.00, 0.06, 0.25, 0.40, 0.58, 0.85, 1.15</td>
<td>2</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.85</td>
<td>0.3, 1, 2, 4, 6, 8</td>
<td>100</td>
</tr>
<tr>
<td>AG Wet</td>
<td>0.00</td>
<td>0.3, 1, 2, 4, 6, 8</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.00, 0.06, 0.40, 0.80, 1.15</td>
<td>2</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>1.25</td>
<td>0.3, 1, 2, 4, 6, 8</td>
<td>100</td>
</tr>
<tr>
<td>Continental Wet</td>
<td>0.00, 0.06, 0.40, 0.80, 1.15</td>
<td>2</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.47</td>
<td>4</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.85</td>
<td>4, 6, 8</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>1.25</td>
<td>0.3, 1, 2</td>
<td>100</td>
</tr>
<tr>
<td>AG Raw Feed Control</td>
<td>0.00, 0.06, 0.40, 0.80, 1.15</td>
<td>2</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>1.25</td>
<td>0.3, 1, 2, 4, 6, 8</td>
<td>100</td>
</tr>
</tbody>
</table>
Carbonation of residues – MSWI

Table 2: Summary of operating conditions for accelerated carbonation of MSWI BA

<table>
<thead>
<tr>
<th>Material type</th>
<th>Carbonation conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO₂ conc.</td>
</tr>
<tr>
<td>MSWI BA</td>
<td>10% vol.</td>
</tr>
<tr>
<td>MSWI BA</td>
<td>100% vol.</td>
</tr>
<tr>
<td>MSWI BA</td>
<td>100% vol.</td>
</tr>
<tr>
<td>MSWI BA</td>
<td>20% vol.</td>
</tr>
<tr>
<td>MSWI BA</td>
<td>20% vol. (CO₂-enriched air)</td>
</tr>
<tr>
<td>MSWI BA</td>
<td>100% vol. (R.H. 65%)</td>
</tr>
<tr>
<td>MSWI BA</td>
<td>0.03% (atmospheric air)</td>
</tr>
<tr>
<td>MSWI BA</td>
<td>100% vol. (water-saturated CO₂ flow)</td>
</tr>
<tr>
<td>MSWI BA</td>
<td>100% vol.</td>
</tr>
<tr>
<td>MSWI BA</td>
<td>100% vol.</td>
</tr>
<tr>
<td>MSWI BA</td>
<td>100% vol.</td>
</tr>
<tr>
<td>MSWI BA</td>
<td>10% vol.</td>
</tr>
<tr>
<td>MSWI BA</td>
<td>20% vol.</td>
</tr>
<tr>
<td>MSWI BA</td>
<td>0.03% (atmospheric air)</td>
</tr>
</tbody>
</table>
# Mineral carbonation – Valuable products

<table>
<thead>
<tr>
<th>Product</th>
<th>Year</th>
<th>Market (Mt/yr)</th>
<th>CO₂ fixed (Mt/yr)</th>
<th>CO₂ source</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMC</td>
<td>1993</td>
<td>0.1</td>
<td>&lt;0.1</td>
<td>Industrial and natural</td>
</tr>
<tr>
<td></td>
<td>1997</td>
<td>0.06</td>
<td>&lt;0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2005</td>
<td>0.1–0.15</td>
<td>&lt;0.1</td>
<td></td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>1979</td>
<td>0.15</td>
<td>&lt;0.1</td>
<td>Industrial and natural</td>
</tr>
<tr>
<td></td>
<td>1996</td>
<td>1.0</td>
<td>~0.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2002</td>
<td>2.6</td>
<td>~0.4</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Product</th>
<th>Year</th>
<th>Market (Mt/yr)</th>
<th>CO₂ fixed (Mt/yr)</th>
<th>CO₂ source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-carbonate</td>
<td>2003</td>
<td>35, ~25% is mined</td>
<td>~15</td>
<td>Partly from limestone</td>
</tr>
<tr>
<td>Na-bicarbonate</td>
<td>2003</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca-carbonate</td>
<td>2005</td>
<td>Several 1000</td>
<td>Mainly mined</td>
<td></td>
</tr>
<tr>
<td>Ca-carbonate PCC</td>
<td>2003</td>
<td>&gt;7</td>
<td>&gt;3.5</td>
<td>Industrial (or natural)</td>
</tr>
<tr>
<td>K-carbonate</td>
<td>2005</td>
<td>0.1–0.2</td>
<td>0.03–0.05</td>
<td>Industrial (or natural)</td>
</tr>
<tr>
<td>K-bicarbonate</td>
<td>2005</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td></td>
</tr>
<tr>
<td>Mg-carbonate</td>
<td>2005</td>
<td>3.5</td>
<td>Mainly mined</td>
<td></td>
</tr>
<tr>
<td>Ba-carbonate</td>
<td>2005</td>
<td>0.02–0.03</td>
<td>~0.01</td>
<td></td>
</tr>
<tr>
<td>Li-carbonate</td>
<td>2003</td>
<td>0.01–0.02</td>
<td>~0.01</td>
<td></td>
</tr>
<tr>
<td>Sr-carbonate</td>
<td>2003</td>
<td>0.3–0.4</td>
<td>~0.1</td>
<td>Soda or coal</td>
</tr>
</tbody>
</table>
Mineral carbonation – Integrated view

Power plant & CO₂ capture → Electricity → Silicates

CO₂ pipeline → Abundant raw materials

Carbonation plant → MgCO₃ and SiO₂

Favourable thermodynamics → Advantages

Mine → Permanent CO₂ storage

Open issues