CO₂ Mineralisation - a scalable & profitable approach to industrial CCS

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CCC is a Cambridge-based, early-stage venture company developing a unique, profitable Mineral Carbonation process to sequester flue-gas CO₂ directly & permanently as magnesium carbonates.
What is Mineral Carbonation?
Earth’s natural carbonate-silicate cycle

Mineral carbonation refers to the conversion of silicates to solid carbonates, mimicking the natural process by which CO₂ is removed from the atmosphere

Wollastonite: CaSiO₃ + CO₂ → CaCO₃ + SiO₂    dH = -90kJ/molCO₂
Olivine: Mg₂SiO₄ + 2CO₂ → 2MgCO₃ + SiO₂    dH = -89kJ/molCO₂
Serpentine: Mg₃Si₂O₅(OH)₄ + 3CO₂ → 3MgCO₃ + 2SiO₂ + 2H₂O    dH = -64kJ/molCO₂

- Primary process by which carbon dioxide is removed from the atmosphere
  >99% world’s carbon reservoir is locked up as limestone & dolomite rock – CaCO₃ & MgCO₃
- Thermodynamically favourable, but kinetically slow

~10¹² tonnes CO₂ in atmosphere

~1 billion tonnes/year CO₂

~10¹⁸ tonnes CO₂ in carbonate rock

OMAN: 70,000km³ of 30% olivine; sufficient to mineralise centuries of global CO₂ emissions.
KEY MESSAGES about CO$_2$ mineralisation

Get the support & enabling policies right & Mineral Carbonation can deliver:

- Commercial deployment of industrial CO$_2$ sequestration, with potential for giga-tonne CO$_2$ scale
- Learning-curve cost reduction through market-driven volume deployment with no/low carbon price
- Economically viable distributed CCS(M) across the range from car & ships to industry & power
- MC opportunity is more about a disruptive alternative to (G)CCS than “using” CO$_2$
- Without targeted R,D&D & policy support, commercial MC will remain niche & not reduce CO$_2$

Situation today – already commercially niche deployed, but in the very slow-lane:

- Niche commercial deployment based on materials valorisation models (even paying for CO$_2$), but very few investors or customers willing to engage with development costs & technical & commercial risks
- Multiple technical approaches with different business models – dangerous to pick “winners”
- Commercial developers & academic researchers are starved of R,D,D&D funding
- Major R&D questions still to be addressed – “downhill” process, but CO$_2$ LCA uncertain
- Increasing academic research, but weakly coordinated & communicated, & little funding

Next-step needs – demonstration funding & industry-academia R&D collaboration:

- Multiple FOAK & NOAK commercial demonstrations required (lots of small projects)
- R&D agenda defined bottom-up by industry needs rather than by top-down CCS policy – economic viability first; CO$_2$ LCA viability second; large-scale CCSM third
- More interdisciplinary R,D&D collaborations; industry partnership critical; funding is critical – process chemists, engineers, modellers, geochemists; mining, metals, minerals, cement, steel, waste, chemicals
- R&D & industry network needed to improve knowledge sharing; more R&D centres = more processes
- Level the playing field with geo-CCS (MC is generally outside scope of CCS programs)
- Policy mechanisms needed to valorise CO$_2$-sequestration independently of emissions reductions
Key R, D & D Challenges – considerable work still to do

• Process engineering design to offset process energy inputs against reaction energy outputs
• LCA to accurately assess net energy usage/output, net CO2 sequestered
• Assessment of capex & opex – expert engineering design studies & demos needed to answer
• New processes that maximise kinetics of both activation of feedstock minerals and of carbonation while minimising energy/chemicals inputs; and avoiding creation of any wastes
  • Modelling of thermodynamics & kinetics of process steps
  • Particular energy intensity issues: evaporation of solvents; crystallisation/recovery of chemicals; sequential consumption of acids and bases
• Electrochemical approaches for both recovery of carbonation energy and chemicals recovery
• Development of processes optimised to use flue gas directly rather than pre-captured CO2
  • More research to investigate kinetics and thermodynamics in gas-solid and aqueous phase carbonation of magnesium (hydr)oxides and salts at low pCO2
  • Effects of flue gas impurities on product qualities
• CCSM potentially involves huge volumes of materials – better understanding of materials qualities, market requirements, volumes and prices needed versus MC process options
  • Processes optimised for different feedstocks
  • Processes optimised for different product outputs
  • Research on effects of seawater as solvent system for large-scale CCSM
  • Processes optimised for different market applications and scales of operation
• Much greater funding needed for interdisciplinary R&D and for multiple commercial demos
  • Process concepts need to be reduced to engineering practice and evaluated at pilot scale
  • Disparate R,D & D activities currently, due to sub-critical, fragmented sector, needs coordination and investment to develop a critical mass of activity; dedicated conferences and journals needed
KEY PERFORMANCE CHARACTERISTICS

Energy & CO2 balance
• Overall energy released = ~70kJ per mole CO₂ sequestered (i.e. ~20% additional to burning coal)
• Energy inputs = to speed up reaction kinetics; to recover chemical reagents (essential to minimise)
• Low-grade energy released, high-grade energy used (essential to recover energy)

Materials Inputs
• Direct dilute flue-gas not pre-captured CO2 (except for in-situ MC & early demonstrations)
• Wastes, minerals & chemicals that contain CaO / MgO (& some other niche options)
• Acids to solubilise Mg, Ca ions (& increase reaction kinetics)
• Alkalis to adjust pH, capture CO₂, precipitate carbonates and/or solubilise silica (& increase kinetics)
• 1-7 tonnes mineral feedstock required per tonne of CO₂ sequestered

Materials Products
• Silica (either combined with low-value carbonate product or separated as pure high-value product)
• Magnesium (or Ca) chemicals (hydroxide, oxide, chloride, sulphate - potential process intermediates)
• Magnesium (or Ca) carbonates (low-grade mixed solids; or high-purity grades; or construction products)
• 2-10 tonnes materials products per tonne of CO₂ sequestered

Materials Values
• Feedstocks: -€100 to +€15 per tonne (-€1000 to +€30 per tonne of CO₂ sequestered)
• Silica: 0-€1000 per tonne (0-€3000 per tonne of CO₂ sequestered)
• Mg/Ca chemical intermediates: 0-€500 per tonne (0-€3000 per tonne of CO₂ sequestered)
• Carbonates: -€5 to +€500 per tonne (-€40 to +€3000 per tonne of CO₂ sequestered)
Business Case: commercial drivers for Mineral Carbonation

negative-value wastes – high-value materials & chemicals products – CO₂ sequestration

- MINERALS & CHEMICALS (Mg, Ca, Fe, Si)
- PROCESSING OF INDUSTRIAL WASTES, NATURAL MINERALS, BRINES, ALKALIS etc.
- ENERGY (chemicals)

- LOW-CARBON MgO & CEMENTS
- METALS RECOVERY
- WASTE REMEDIATION

- CARBONATE PRODUCTS
- REACTIONS WITH EXHAUST GASES (CO₂, SOx, NOx), AIR, CO₂ or FUELS
- (wastes) ENERGY

- CO₂ SEQUESTRATION
- STABILISED WASTES
- ZERO-CARBON CONSTRUCTION MATERIALS

- Alcoa: red mud waste stabilisation
- C8S: APC wastes to building blocks
- CCC: olivine-to-Mg(OH)₂ & SiO₂ for scalable CCS
Mineral Carbonation versus Geological CCS

Mineral carbonation is an energy-generating & scalable CO₂-sequestration alternative to the capture, separation, purification, compression, transport and storage of gaseous/liquefied CO₂ that is associated with geo-CCS.

- 30% cost and energy penalty
- More expensive than nuclear or on-shore wind; infrastructure dependent
- Estimated €40-90/tonne* CO₂ versus lower ETS price
- Public acceptance issues
- Relatively well developed & demonstrated technology

✓ Stand-alone without CO2 infrastructure
✓ Stable, safe solid products
✓ Product materials are commercially useful
✓ Wastes can be used as inputs
✓ Already commercially deployed in niche applications without CO2 price
× energy intensive mineral processing steps
× Huge materials volumes to handle/sell/store

* Source: McKinsey
Giga-tonnes of Carbonate products – where would they all go?

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*very approximate market data

*source: Calera, 2009
Ex-Situ Mineral Carbonation – multiple technical approaches*

*source: Torrontigue, ETH Zurich, MSc 2010
Mineral Carbonation - a range of technical approaches & 20yrs R&D

- Essentially: $\text{CO}_2 + \text{source Ca/Mg/Fe} = \text{limestone / HCO}_3^-$
  - pH, temperature, water, pCO2, source: phase, chemistry, size
  - exothermic, but more energy is needed to overcome kinetics
  - wastes much easier than natural rocks, but rocks more available than wastes
  - Ca much easier than Mg, but Mg (serpentine, olivine, brines) more available than Ca (wollastonite, brines)

- Gas-solid phase reactions (easiest, most developed, commercial operations):
  - mill to <75um, heat ~650°C and/or acid/base digestion (~100°C) required to activate serpentine for carbonation; pure $\text{CO}_2(g)$ + activated serpentine = aggregates (slow & energy intensive)
  - dilute $\text{CO}_2(g)$ + combustion ashes = aggregates + heat (very easy, but not scalable)
  - mine tailings: natural atmospheric carbonation 1-50 kt/$\text{CO}_2$/yr per mine site – rate-limited by silicate mineral dissolution & depends on local climate [Dipple, 2009 - study at four Canadian & Australian sites]

- Aqueous-phase (lowest energy, less developed, +chemicals, attractive economics):
  - chemical activation/digestion of silicates or wastes to generate Ca/Mg salts or ions
  - brines & liquid waste sources of Ca/Mg ions
  - direct capture of CO2 from flue gases into alkaline solution, brines & Mg(OH)$_2$
  - selective precipitation of product carbonates & by-products & cementitious phases
  - overall: $\text{CO}_2 + \text{water(high pH)} + \text{Ca/Mg salts} = (\text{bi})\text{carbonates} + \text{silica} + \text{residual metals} (\text{typically \sim 80-150°C} & \text{ambient to high-pressure})$
  - closed-cycle, pH-swing ammonium bisulphate digestion at 80°C & carbonation to convert $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ to high-purity MgCO$_3$, SiO$_2$ & Fe
  - direct NaOH or KOH digestion of silicates to form solid Mg(OH)$_2$ & Ca(OH)$_2$
Mineral Carbonation - small R&D base, but increasing activity

*source: Torrontigue, ETH Zurich, MSc 2010*
Some Commercial Activities in Mineral Carbonation

Economic feasibility is (slowly) driving worldwide Mineral Carbonation development

- **China Huaneng & Peabody** – Xiliguole (Mongolia) 1.2GWe supercritical coal using mineral carbonation (Calera technology) coupled to local building materials production
- **UK ETI** – £1m 2011-13 study on “mineralisation opportunities” (Shell, Caterpillar, BGS, CICCS)
- **USDoE** – CO₂ Mineral Sequestration working group: (ARU, ASU, LANL, NETL, PSU, SAIC, UU)
- **Shell** – 8yrs development of a flue-gas de-carbonation slurry process: heat/steam-activated serpentine powder in slurry to strip CO₂ then heat & pressure & separate carbonate solids
- **Alcoa** – Kwinana commercial plant carbonating red mud slurry waste to reduce storage costs
- **Carbon Sense Solutions** – Canadian manufacturer using CO₂ to fast-cure building blocks
- **EnPro** – developing 24,000tonne CO₂/yr capture into alkaline wastes project in Norway.
- **Calera** – early VC-backed California start-up developing commercial carbonation of waste hydroxides & brines; low-energy electrolysis of brine to create base for CO₂ capture; focused on selling/qualifying products for cement and construction industry; Australia (Latrobe) & Mongolia
- **Skyonic** – building $25m Texas pilot plant to capture flue gas to convert sodium hydroxide (optionally via electrolysis) to NaHCO₃ (dried product for sale); life-cycle CO₂ unclear
- **Carbon8** – UK venture with simple profitable process for conversion of low-pressure CO₂ to building aggregate by direct carbonation of wet mix of hazardous APC wastes + quarry fines
- **Cambridge Carbon Capture** – CO₂ sequestration via olivine-to-brucite & silica; CO₂ fuel cell
- **Cquestrate / Oxford Geo-Engineering** – focused on net CO₂ capture from atmosphere as ocean bicarbonate via liming of oceans
- **Integrated Carbon Sequestration Ltd** – Australian developer of flue-gas de-carbonation via ammonia + activated serpentine (similar to Shell)
- **Others** – **Novacem** (Mg cement), **Calix** (MC materials), **GreenMag** (processes), **Oman** projects
(Some) UK R&D Activities in CO2 Utilisation via Mineral Carbonation

- **ETI** – £1m 2011-13 study on “mineralisation opportunities” (Shell, Caterpillar, BGS, CICCS)
- **Shell** – 8yrs development of a flue-gas de-carbonation slurry process: heat/steam-activated serpentine powder in slurry to strip CO₂ then heat & pressure & separate carbonate solids
- **Nottingham University & BGS** - partnership on CCS R&D with strong component of mineral carbonation science; recent partner with ETI mineral carbonation project
- **Greenwich University** – £1m award (2013) for EU collaborative project on carbonation of wastes
- **Carbon8** – UK venture (spin-out of Greenwich) building second commercial mineral carbonation plant (building blocks made via low-pCO₂ carbonation of hazardous wastes)
- **Cambridge Carbon Capture** – CO2 sequestration via olivine-to-brucite & silica; CO2 fuel cell
- **Oxford University / Cquestrate** – open source collaboration focused on net CO₂ capture from atmosphere as ocean bicarbonate via liming of oceans
- **Southampton University** – growing strong team in mineral carbonation; in-situ & ex-situ and ocean processes
- **Herriot Watt** – new centre of expertise in CCSM R&D with recruitment of Prof Maroto-Valer
- **Sheffield University** – R&D in cement, waste and olivine carbonation processes
- **Cambridge University** – olivine-to-brucite process; also carbonate looping
- **Novacem (Imperial spin-out)** – CO2 sequestration via magnesia cements; significant early-stage developer with industrial partners, recently went bust & assets acquired by Calix
- **Conoco Philips, BP** – major investors in Skyonic (building mineral carbonation plant in Texas)
- **Newcastle University** – novel bio-catalysis of aq-phase mineral carbonation
- **Others** – Leeds, Birmingham, West of Scotland, Arup, MIRO, Sibelco, & more…
**CCC process schematic – digestion step 1**
(alkaline digestion of serpentine or olivine to convert to brucite & silica)

**USP: profitable, low-energy, silicate digestion process**

**PROCESS COSTS:**

€12 0.8t olivine
€105 0.5t NaOH (/tCO₂ sequestered)

**MINERAL MINE**

**INDUSTRIAL WASTE**

**TRACE METALS**

€19 .2%Ni

**Overall:** \( \text{Mg}_2\text{SiO}_4 + 2\text{H}_2\text{O} \Rightarrow 2\text{Mg(OH)}_2 + \text{SiO}_2 \quad \text{dH}=-12kJ \quad \text{dG}=+9kJ \)

1. \( \text{Mg}_2\text{SiO}_4 + 2\text{NaOH} + \text{H}_2\text{O} \Rightarrow 2\text{Mg(OH)}_2 + \text{Na}_2\text{SiO}_3 \quad \text{dH}=-115kJ; \quad \text{dG}=-68kJ \)

2. \( 2\text{Na}^+ + \text{SiO}_2(\text{OH})_2^{2-} \Leftrightarrow \text{SiO}_2(\text{ppt}) + 2\text{Na}^+ + 2\text{OH}^- \quad \text{dH}=+12kJ; \quad \text{dG}=+5kJ \)

*€133* 0.7t \( \text{Mg(OH)}_2 \)

*€12* heat

*€174* 0.7t \( \text{Na}_2\text{SiO}_4 \)

*€19* .2%Ni

*€205* 0.3t APS

**Precipitation of silica & trace metals recovery**

**Separation of Mg(OH)₂ from alkali silicate (aq. filtration)**

**Digestion of mineral silicates (180°C, 1 atm, 3hrs)**

**NaOH re-cycle**

**energy**

**water re-cycle**

**INDUSTRIAL WASTE**

**MINERAL MINE**

**TRACE METALS**
CCC Process: Olivine-to-Brucite conversion at high-pH

Before Digestion

After Digestion

single-step, fast, low-energy conversion of magnesium silicate to magnesium hydroxide e.g. low-carbon alternative to portlandite

~92wt% Mg$_2$SiO$_3$
(1mole, ~141g)

~80 wt% Mg(OH)$_2$
(0.8mole, ~47g)
CCC process schematic – carbonation step 2
(direct carbonation of brucite (magnesium hydroxide) with flue-gas into ocean or products)

Overall: \[2\text{Mg(OH)}_2 + 4\text{CO}_2 \rightarrow 2\text{Mg(HCO}_3\text{)}_2\quad \text{dH}=-268\text{kJ} \quad \text{dG}=-140\text{kJ}\]

1. \[4\text{CO}_2 + 4\text{OH}^- \rightarrow 4\text{HCO}_3^- \]
2. \[2\text{Mg(OH)}_2 + 4\text{HCO}_3^- \rightarrow 2\text{Mg(HCO}_3\text{)}_2 + 4\text{OH}^- \]

Diesel exhaust

Mg(OH)$_2$  

(€133) 0.7t

Sequestration via formation of soluble magnesium bicarbonate in seawater (or reaction to solid MgCO$_3$)

Heat, or CARBON-FREE ELECTRICITY via FUEL CELL

Mg(HCO$_3$)$_2$ SOLUTION

€35 1t CO$_2$

MgCO$_3$ Powder

€192 1t

USP: “zero-carbon”, “zero-cost” permanent CO$_2$ capture & storage
Electrochemical Mineral Carbonation – option for carbonation step 2
(energy of carbonation recovered as carbon-negative electricity via direct CO2 fuel cell)

**the direct CO\(_2\) fuel cell:**  
\[ \text{Mg(OH)}_2 + \text{CO}_2 \rightarrow \text{MgCO}_3 + \text{H}_2\text{O} \]  
\[ E_{\text{cell(stand)}} = 0.44\text{V} \]  

4. \[ \text{Mg(OH)}_2(\text{aq}) + \text{CO}_3^{2-} \rightarrow \]  
\[ \text{MgCO}_3(\text{s}) + \text{H}_2\text{O} + 0.5\text{O}_2 + 2\text{e}^- \]

3. \[ \text{CO}_2(\text{g}) + 0.5\text{O}_2(\text{g}) + 2\text{e}^- \rightarrow \text{CO}_3^{2-} \]

\( \text{CO}_2 \) can be a fuel to generate electricity
KEY MESSAGES …again

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- Policy mechanisms needed to valorise CO$_2$-sequestration independently of emissions reductions
“CCC objective: to develop, deploy & operate profitable solutions for industrial customers to permanently sequester CO₂ via conversion of wastes into valuable minerals, metals & zero-carbon electricity”

- University of Cambridge – Depts Materials Science & Metallurgy; Engineering
- University of Nottingham – Centre of Innovation in CCS
- University of Sheffield – Dept. Materials Science & Engineering
- University of Greenwich – School of Science

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