

CO₂ fixation by serpentinite

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Overview

- Background and scope
 - CO₂ mineral sequestration
 - The ÅA route for stepwise serpentinite carbonation
- Progress / results since 2006
 - Mg(OH)₂ production from magnesium silicate-based rock
 - Mg(OH)₂ carbonation
 - Process energy requirements
 - Avoid CO₂ capture: direct operation on flue gas
- Conclusions



CCUS* in / for Finland

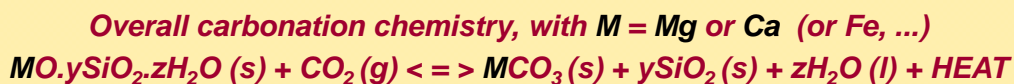
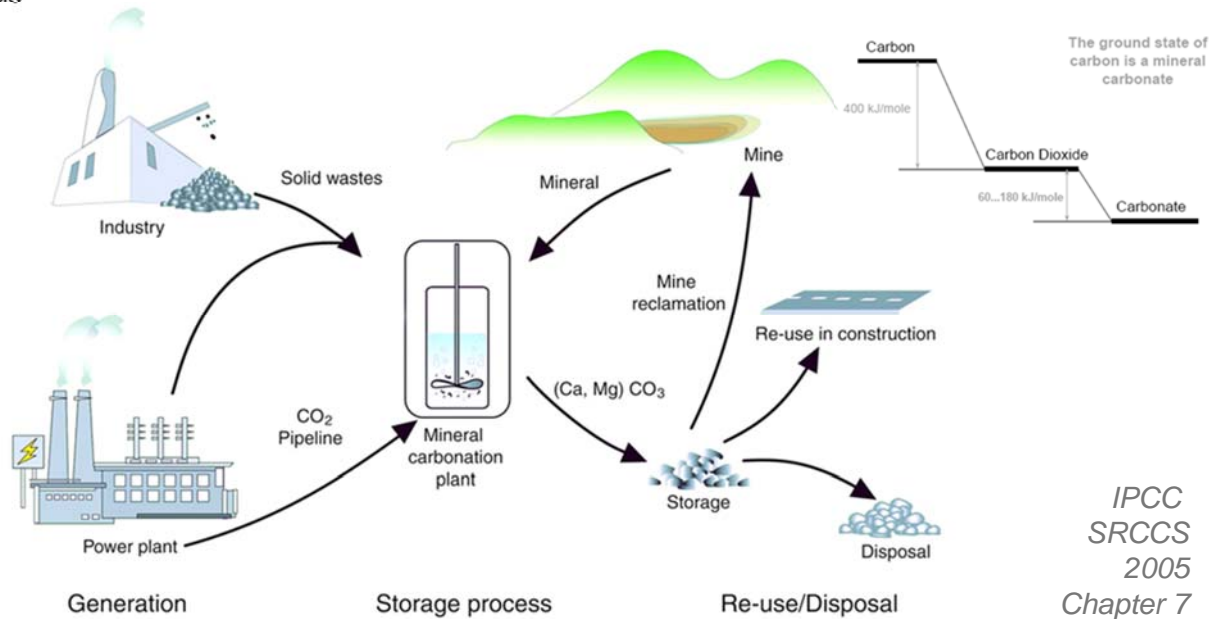
earlier:
"CCS"
↑
↓
"CCU"

	In Finland	Near Finland / abroad
Geological storage	Not possible	Baltic sea ?
Ocean storage	Not possible	Not possible
Mineral sequestration	Large potential Projects ongoing	Projects ongoing PT, SG, LT, (CA?, ZA?)
CO₂ utilisation	Several applications (PCC, CO ₂ solvent...) Projects ongoing	Projects ongoing US

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



CO₂ mineralization: what, how



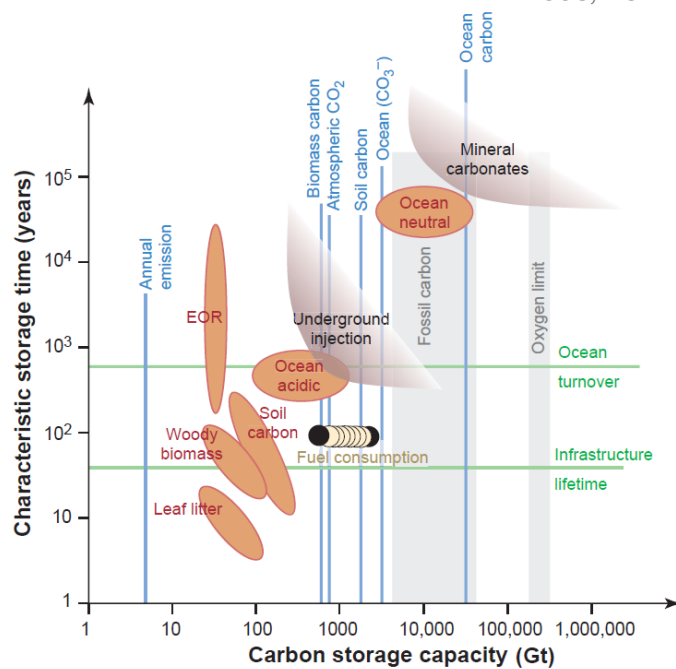
CO₂ mineralization potential

Lackner,
Science vol. 300,
2003, 1677-1678

- 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



Muscat: surrounded by ultramafic rocks



Persian Gulf and the Oman Ophiolite

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

Kelemen & Matter, PNAS 2008)



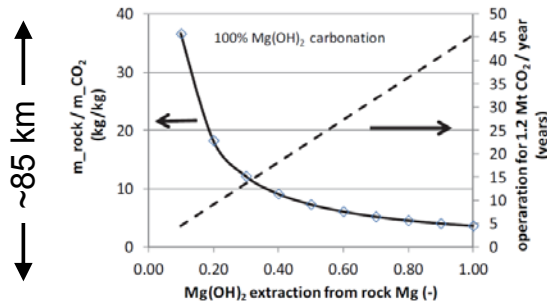
Pictures:
R Hunwick
Presented in Sydney,
March 12, 2012



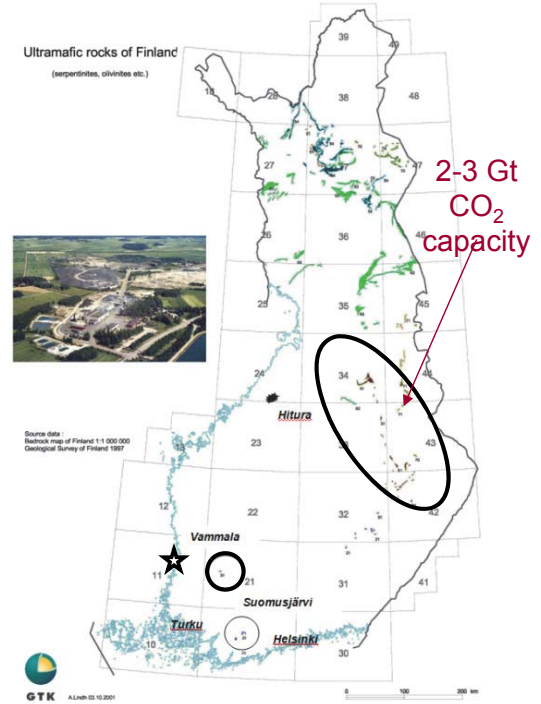
Mineral resources; source-sink links

For example for Finland:

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



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



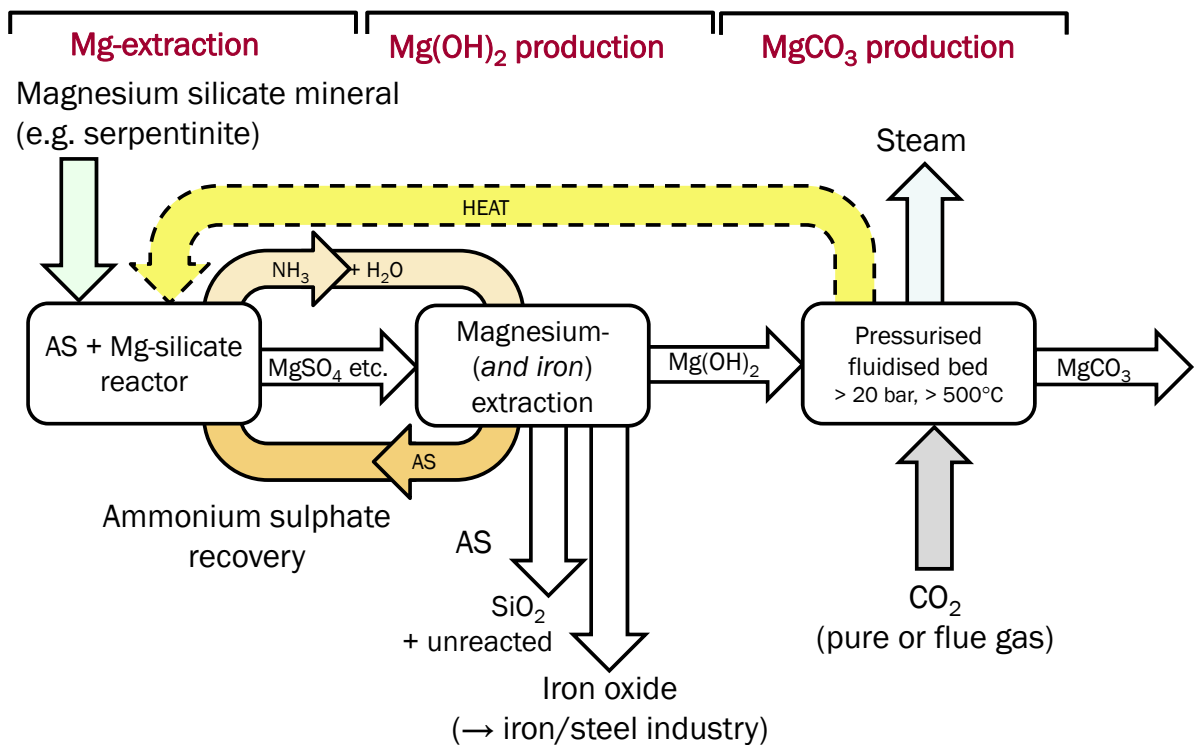
Zevenhoven et al. ECOS2012

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

	MgO	CaO	Fe ₂ O ₃ *	SiO ₂	Al ₂ O ₃	Other
Hitura (FI)	36.2	0.5	14.4	24.8	<0.1	24.1
Ni-ore Hitura (FI)	28.5	0.6	15.9	33.9	2.0	19.1 (NiO 1.0)
Vammala (FI)	19.2 – 28.0	1.4 - 90	15.4 – 18.4	39.3 – 46.9	1.3 – 3.5	7.9 – 11.6
Suomensjärvi (FI)	13.5 – 20.9	7.8 – 8.3	10.9 – 11.9	44.3 – 50.2	7.0 – 10.8	6.8 – 7.6
NSW Grt Serp belt (AU)	38.1	0.05	6.9	41.8	1.0	12.1
Bragança 7 fontes (PT)	35.8	0.02	8.2	41.9	1.2	12.8
Bragança Donai (PT)	36.7	0.25	7.29	42.7	1.6	11.5
Varena (LT)	25.5 – 35.4	0.21 – 2.5	14.1 – 33.6	28.8 – 37.2	0.11 – 1.8	9.5 – 15.0

* Calculated, presumably a mixture of FeO and Fe₂O₃, partly (?) Fe₃O₄.

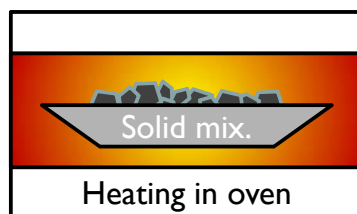
Mg-silicate carbonation: the ÅA route



Test methods @ ÅA 2007 →

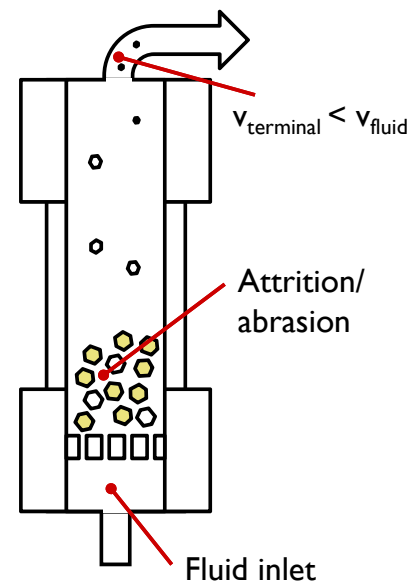
1. Mg(OH)₂ production

- Mixing serpentinite and AS
- Heating (<450°C)

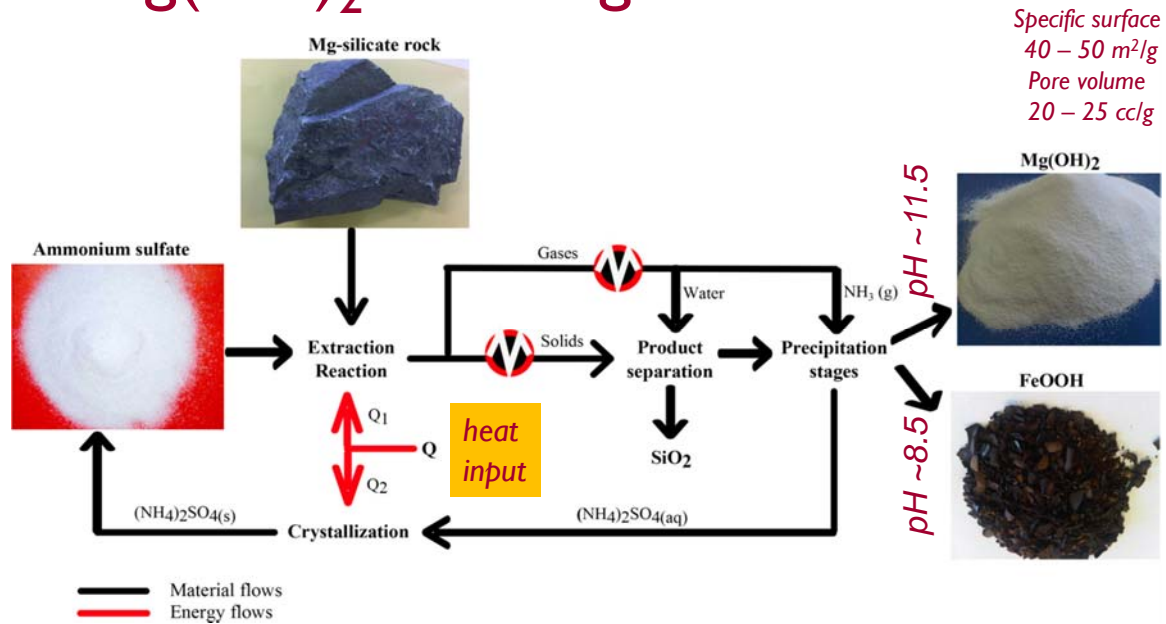


- Dissolution of MgSO₄ and precipitation of Mg(OH)₂ from aqueous solution
- Regeneration of AS salt

2. MgCO₃ production

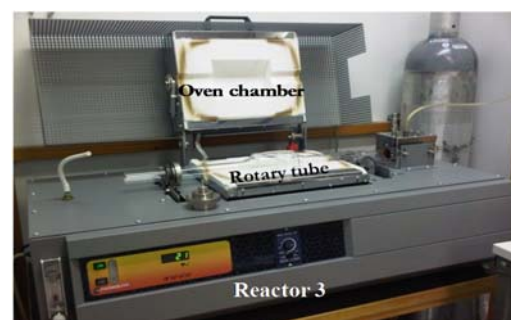
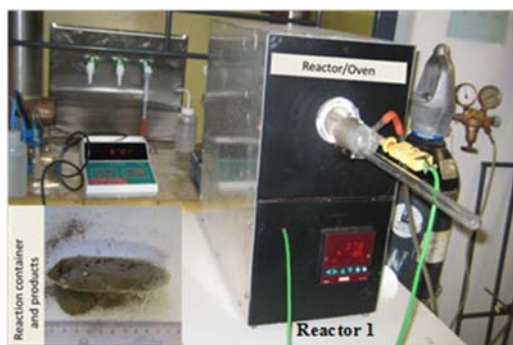


Closed loop process producing $Mg(OH)_2$ from Mg-silicate rock



Nduagu, dr. thesis ÅA 2012

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

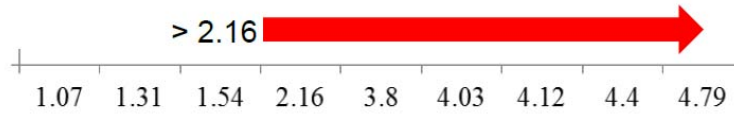


- Tested:**
- 1) dry / wet samples
 - 2) mixing / no mixing
 - 3) layered / pre-mixed
 - 4) Al / ceramic sample holder
 - 5) Ammonium sulphate/ bisulphate

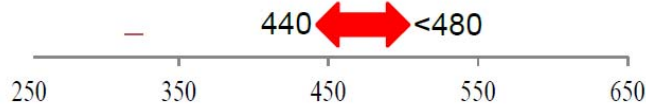
Nduagu, dr. thesis ÅA 2012

Summary for Mg(OH)₂ production

Rock type
Serpentinites
(Mg/Fe ratio)

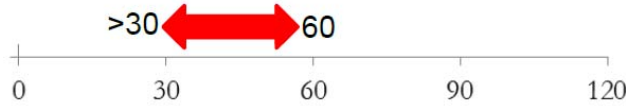


Temperature
(°C)

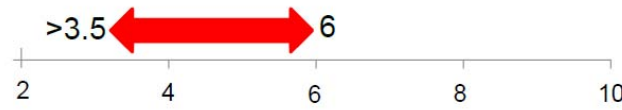


*Preferably
max 400°C*

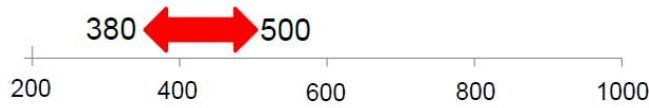
Time
(min)



Process energy
GJ/t-CO₂



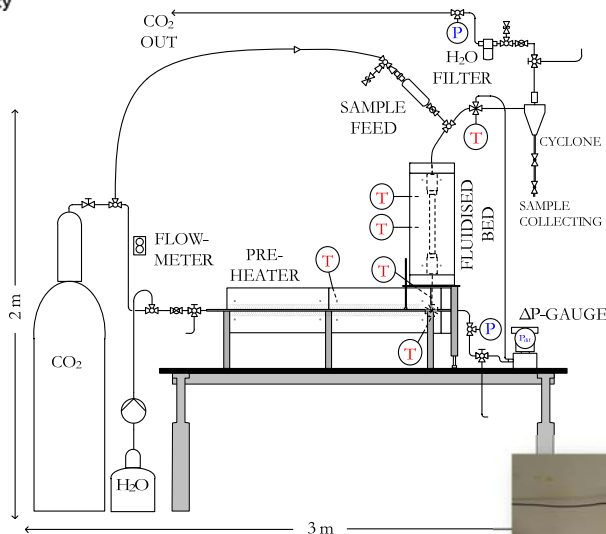
GHG footprint
kg-CO₂e/t-CO₂



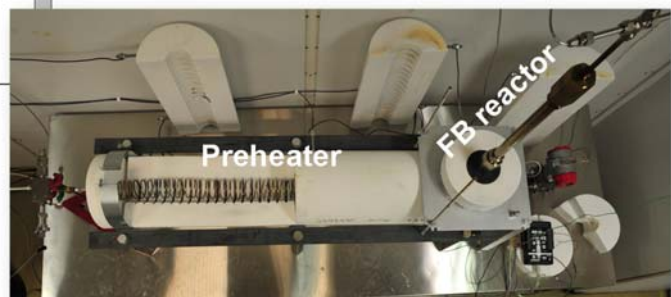
Nduagu
PhD thesis
defence
lectio
13.12.12



The pressurised fluidised bed @ ÅA



2008-2011



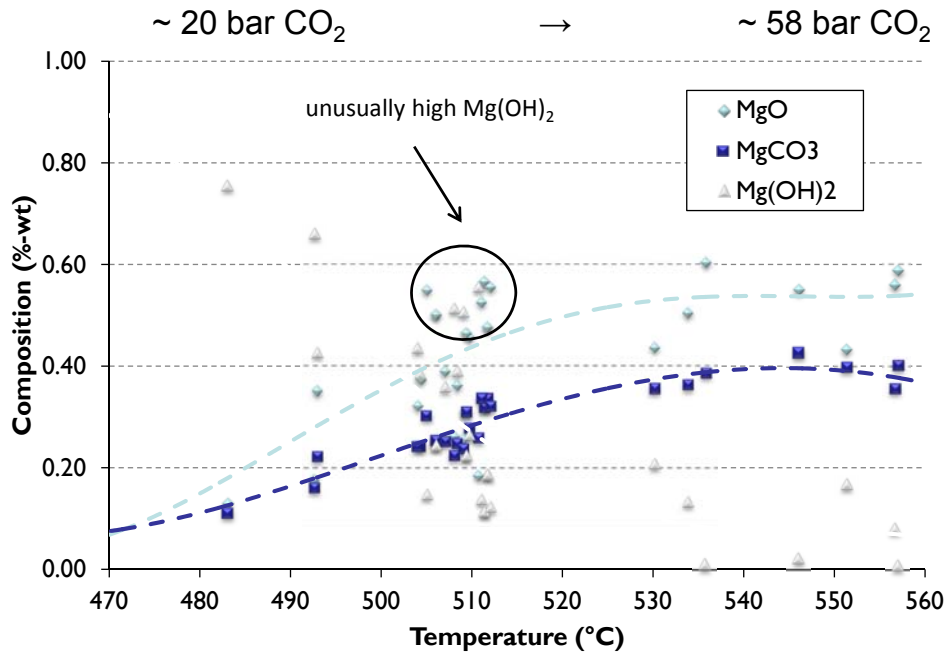
Research questions:

- 1) No build-up of MgCO₃ on Mg(OH)₂ particles?
- 2) Fast kinetics?
- 3) What about supercritical CO₂?



Mg(OH)₂ carbonation – results

using commercial Dead Sea Periclase material (BET ~ 5 - 8 m²/g)

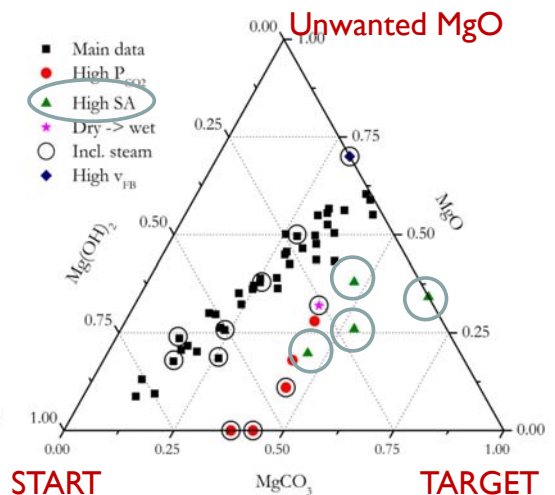
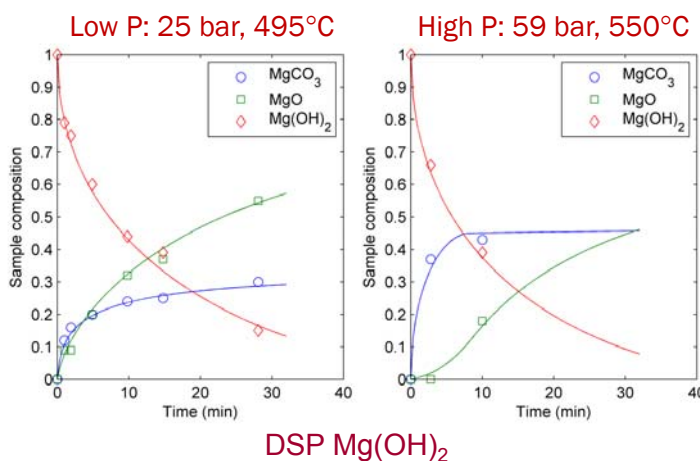


scCO₂:
no
advantage
(tests up to
~80 bar)

Fagerlund 2009, 2010



PFB carbonation of Mg(OH)₂

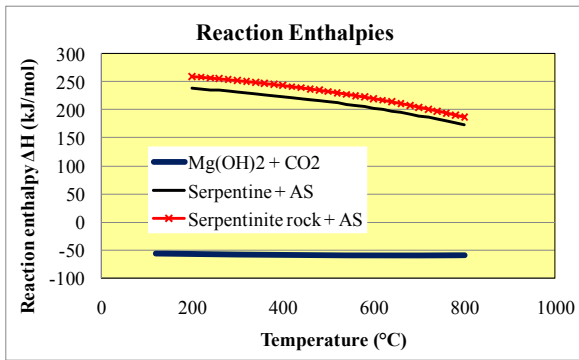


- Competition between dehydroxylation and carbonation
 - Own-produced Mg(OH)₂ has good quality (green triangles)
 - Optimise Mg(OH)₂ precipitation conditions, control properties

Fagerlund, dr. thesis ÅA 2012



Process energy requirements

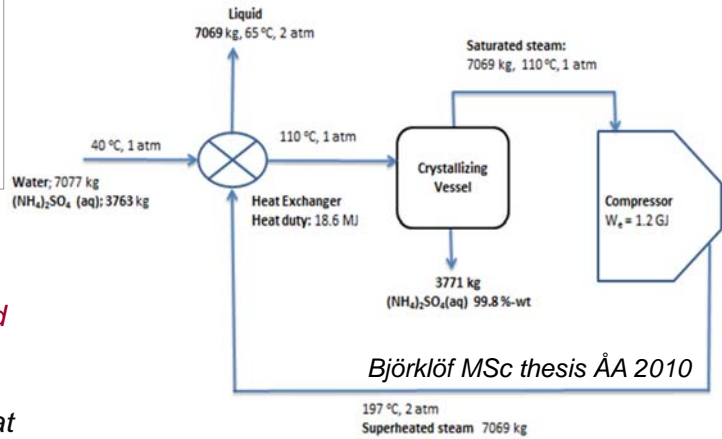


Reaction enthalpies vs. temperature for extraction of 1 mol of Mg from pure serpentine or from Finnish serpentinite, and for the carbonation.

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

Mechanical vapour recompression (MVR) crystallization of AS salt

MVR compression work ~1.2 GJ/t CO₂

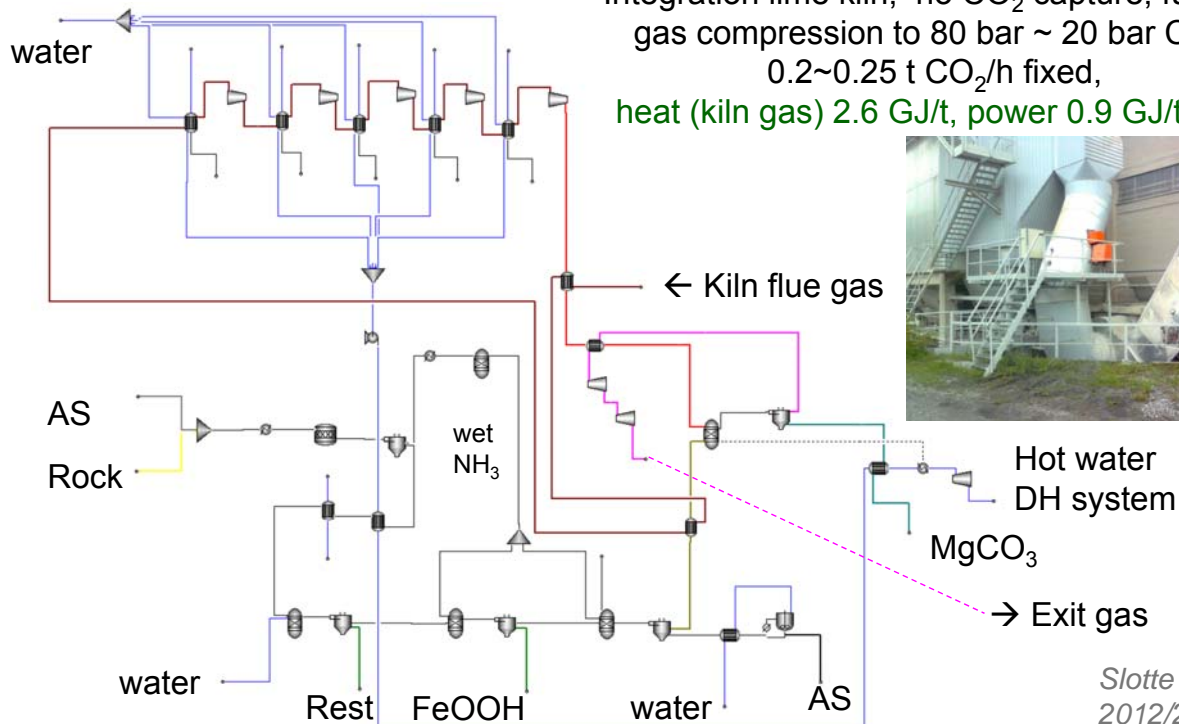


Total penalty ~3 GJ (mainly 400°C heat) and ~3 t rock per ton (1000 kg) CO₂

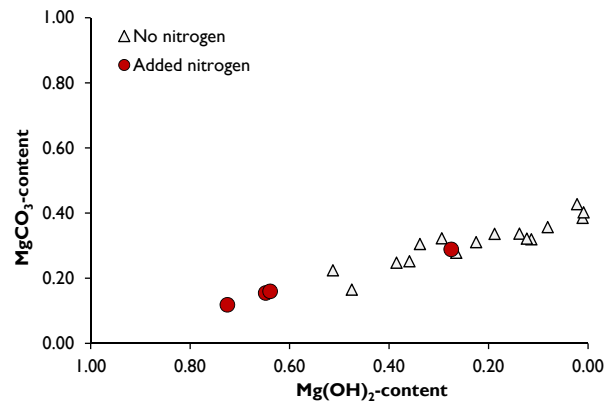
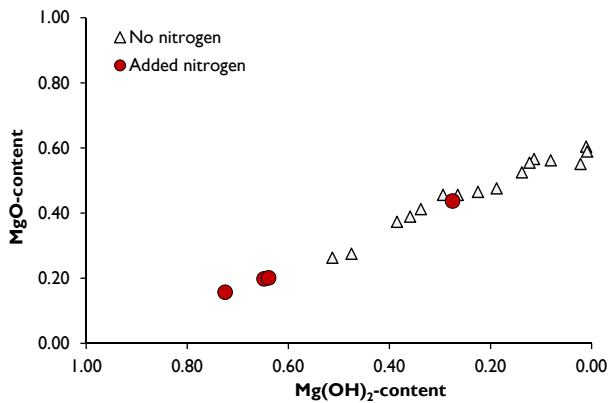


Optional: application at a lime kiln 2013

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



Conversion of $\text{Mg}(\text{OH})_2$ to MgCO_3 and MgO in (wet) CO_2 or CO_2 diluted with (26-72%) N_2 .



Total pressure 10 – 59 bar, temperature 450 - 550°C, time 15 minutes
Dead Sea Periclase (DSP) $\text{Mg}(\text{OH})_2$, 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) $\text{Mg}(\text{OH})_2$ carbonation ~65%
- Energy input ÅA route so far ~3 GJ/t, $\approx \text{CO}_2$ capture from NG
- Challenge: $\text{Mg}(\text{rock}) \rightarrow \text{Mg}(\text{OH})_2 > 90\%$ & "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 ?!

