ETH zürich

Research on the direct mineralization of flue gas CO_2 at ETH Zurich

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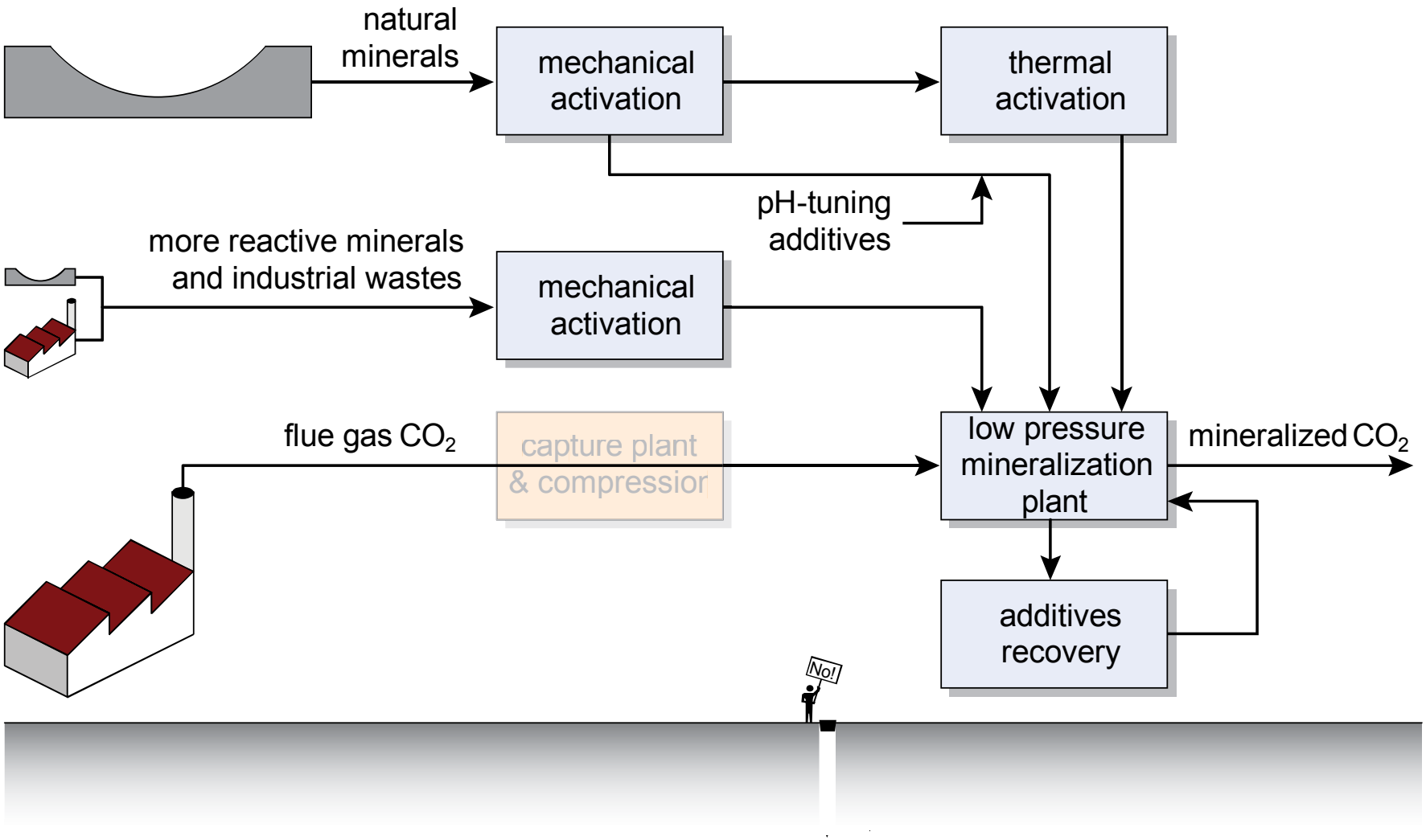
Institute of Process Engineering

Alternative CCS Pathways Workshop
Oxford, June 26-27 2014

Direct flue gas CO_2 mineralization – Motivation



Direct flue gas CO_2 mineralization – Activation

- Capture integration should allow to **intensify the pretreatment** of precursor material

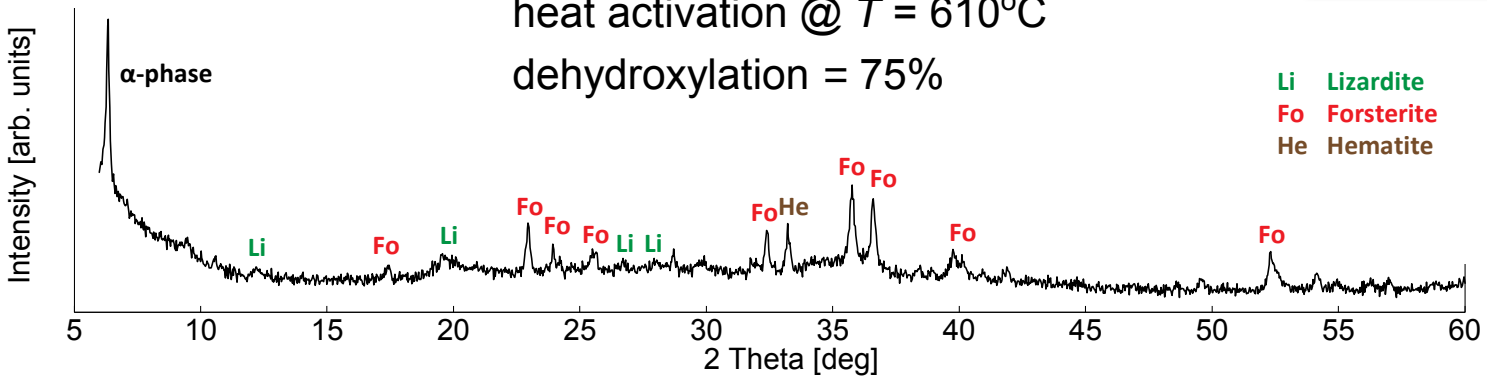
Mechanical & thermal activation of lizardite

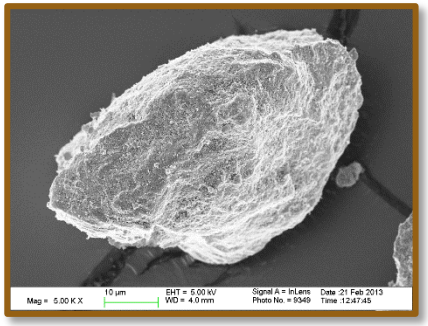
$$Mg_3Si_2O_5(OH)_4 \longrightarrow Mg_3Si_2O_{6.5}(OH) + 1.5H_2O$$

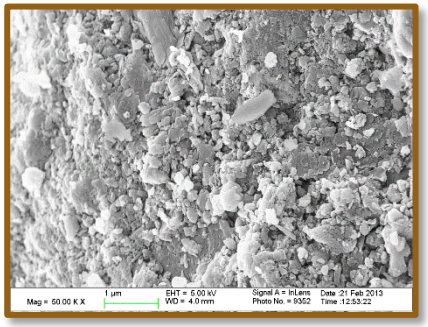
particle size = -125 µm

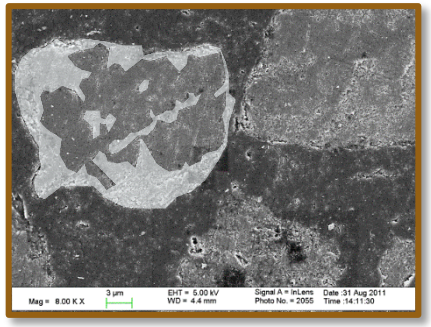
heat activation @ T = 610°C

dehydroxylation = 75%



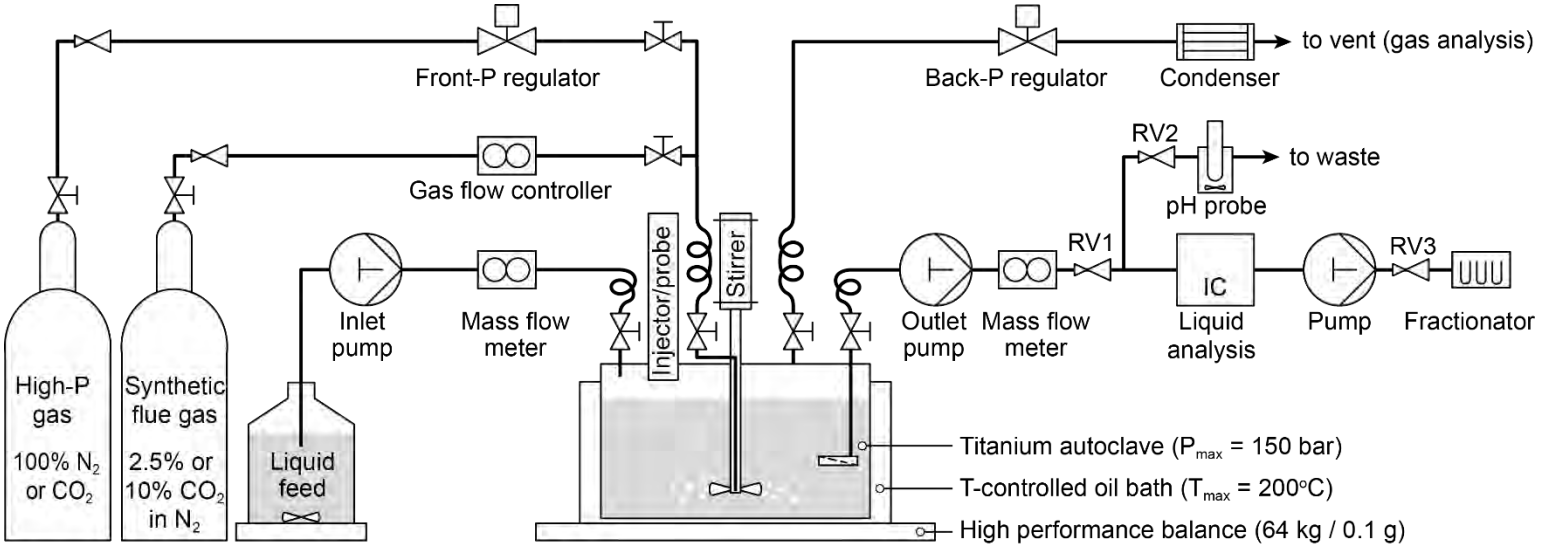


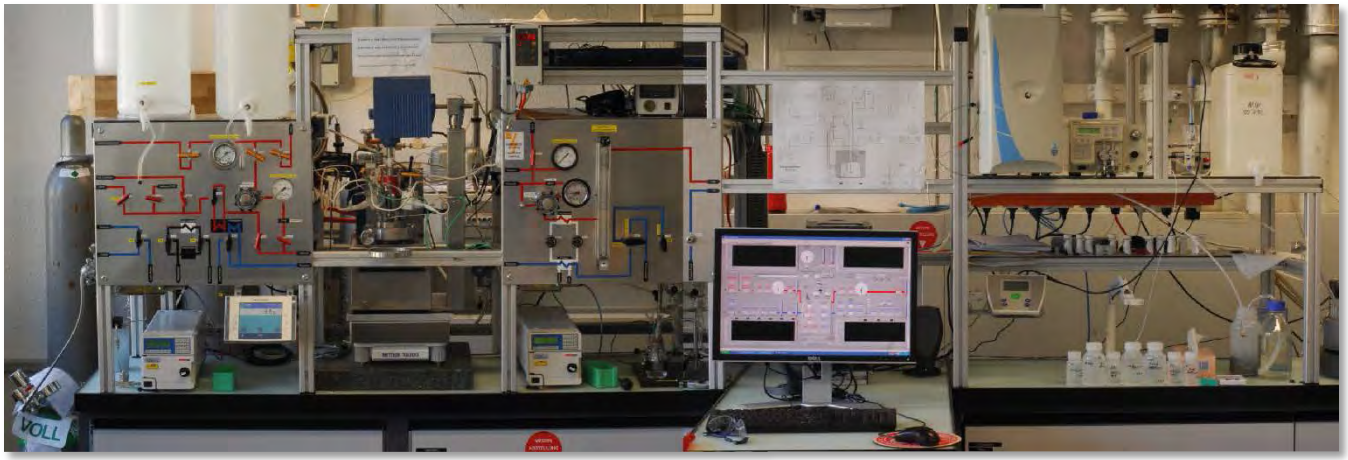




Direct flue gas CO_2 mineralization – Dissolution

- Parametric study on activated serpentine dissolution: **Liquid** and **gas flow-through setup**



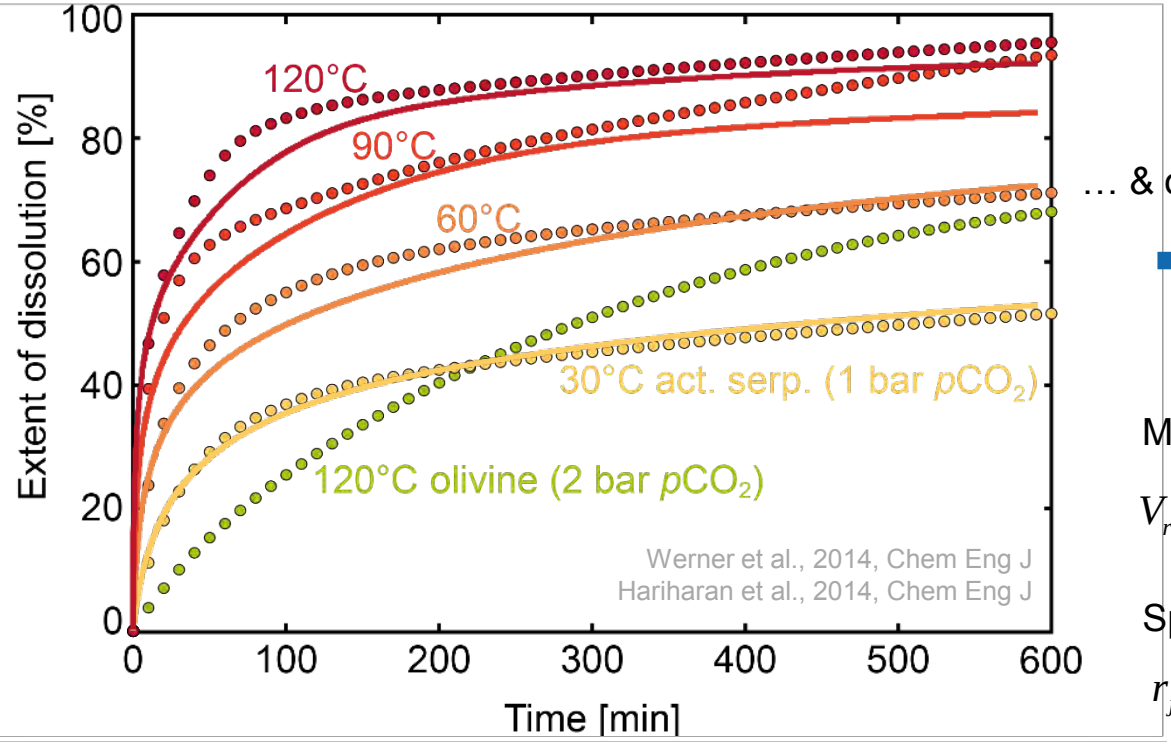


Werner et al., 2014, Chem Eng J

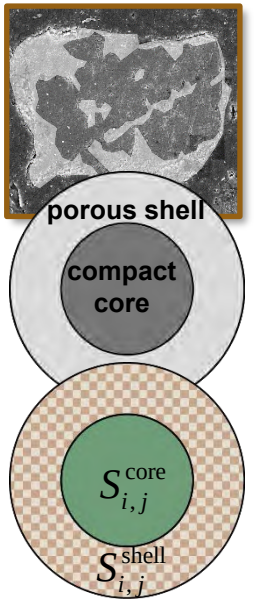
Direct flue gas CO_2 mineralization – Dissolution

- **Parametric study** on activated serpentine dissolution and **kinetic modeling**

lean *T* **lean *p*CO_2**



Alteration of physical morphology…



→ Multiple layers in a particle ***i*** :

… & of chemical compostition:

→ Multiple dissolving species ***j*** :

Material balance for solute ***k*** (Mg or Si):

$$V_r \frac{dc_k}{dt} = \sum_i \sum_j \left(\nu_{j,k} \left(S_{i,j}^{shell} + S_{i,j}^{core} \right) r_j \right) - Q c_k$$

Specific dissolution rates r_j :

$$r_j = f(T, pH)$$

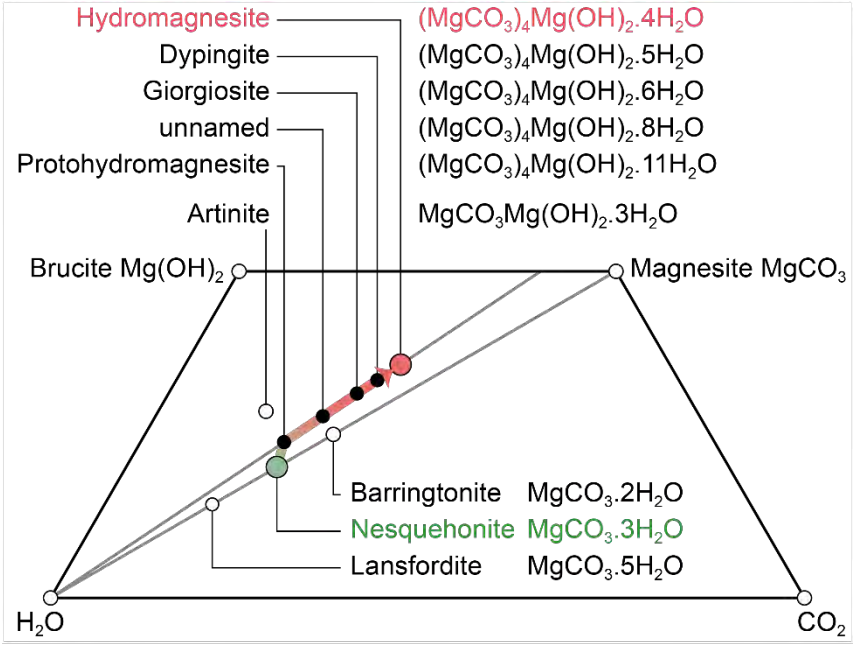
→ Speciation model

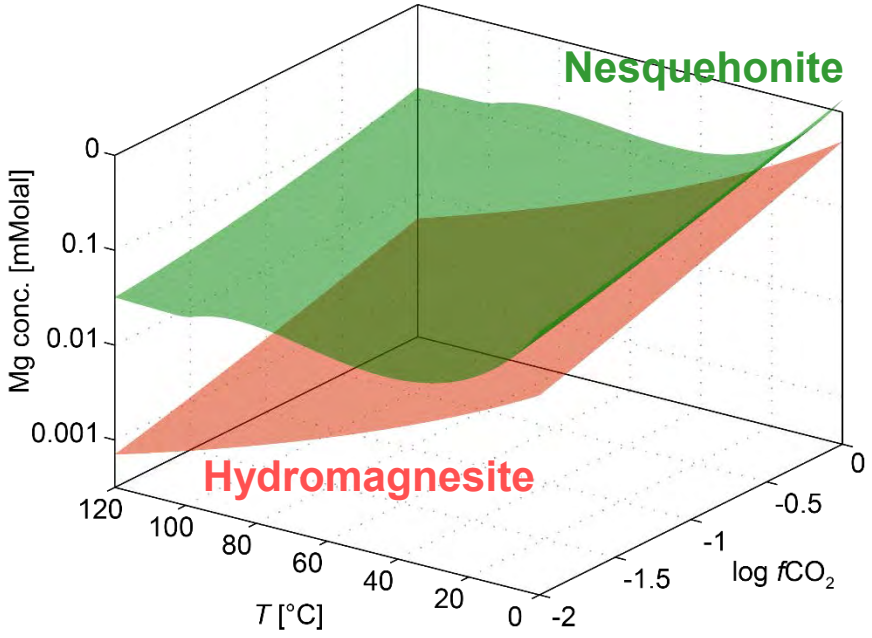
→ Surface complexation model

- **>80% in 100 min**: activated serpentine dissolves rapidly even at lean *T* and *p*CO_2

Direct flue gas CO_2 mineralization – Precipitation

- Ternary phase diagram for the **$MgO–CO_2–H_2O$ system** and solubility surfaces



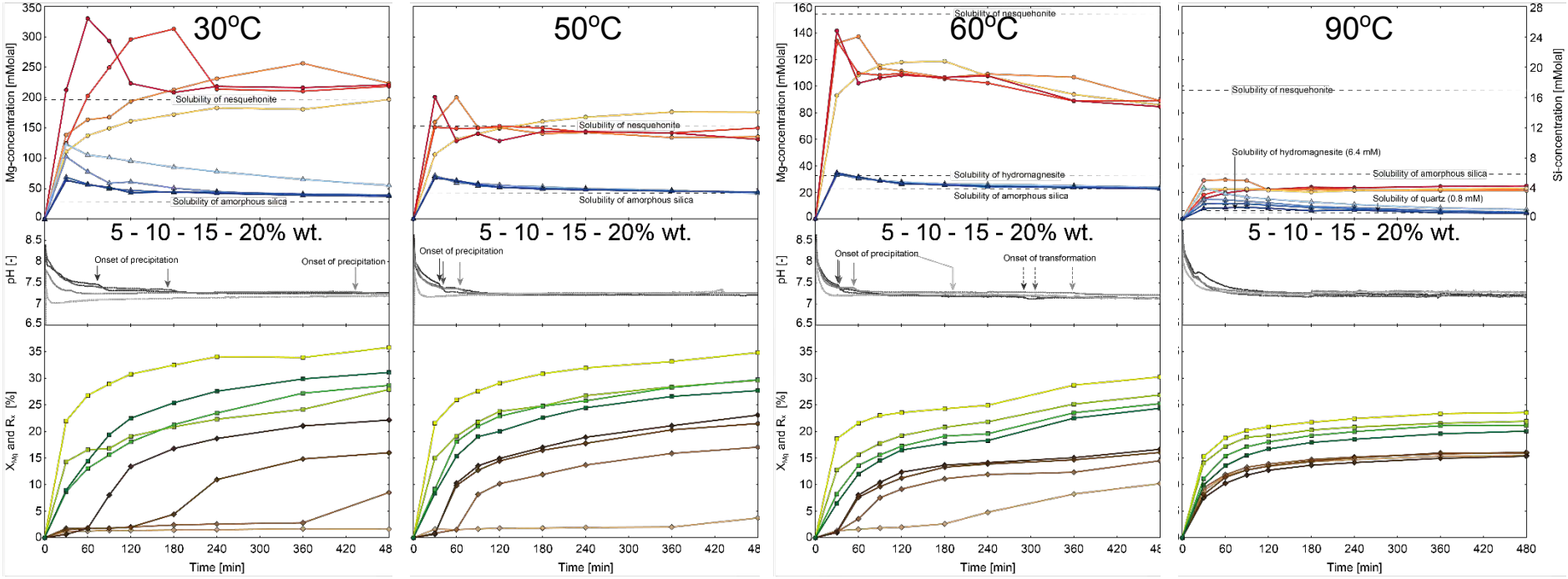


- Change from precipiation of **a more soluble carbonate at lower *T*** to the formation of a **less soluble** but thermo-dyn. more stable **carbonate at higher *T***

Direct flue gas CO_2 mineralization – Carbonation

Fast forward ▶▶

- **Parametric study** (*T*, solid/liquid ratio) in single-step batch mode



Werner et al., Phys Chem Chem Phys, submitted

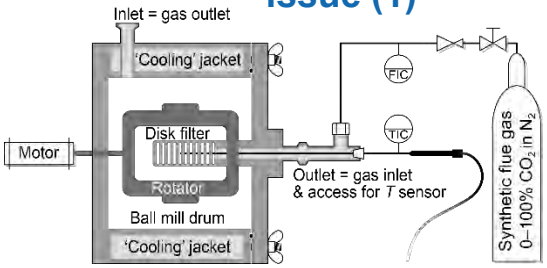
Direct flue gas CO_2 mineralization – Carbonation

Fast forward ▶▶

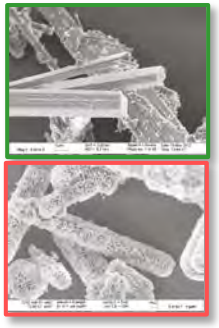
- **Parametric study** (*T*, solid/liquid ratio) in single-step batch mode
  - ➡ Insight into precipitation regime in the aS–CO_2–H_2O system
  - ➡ **(1) Mg & Si re-precipiation** and **(2) equilibrium effects** hinder reaction progress

- Investigation of possible improvements:

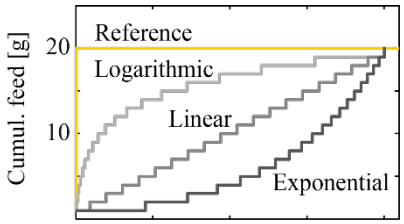
Concurrent grinding
issue (1)



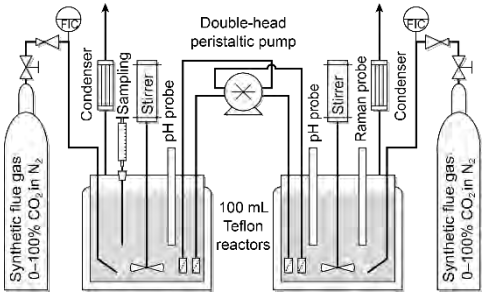
Carbonate seeding
issue (1)



Sequential feed addition
issue (2)



Double-step carbonation
issue (2)

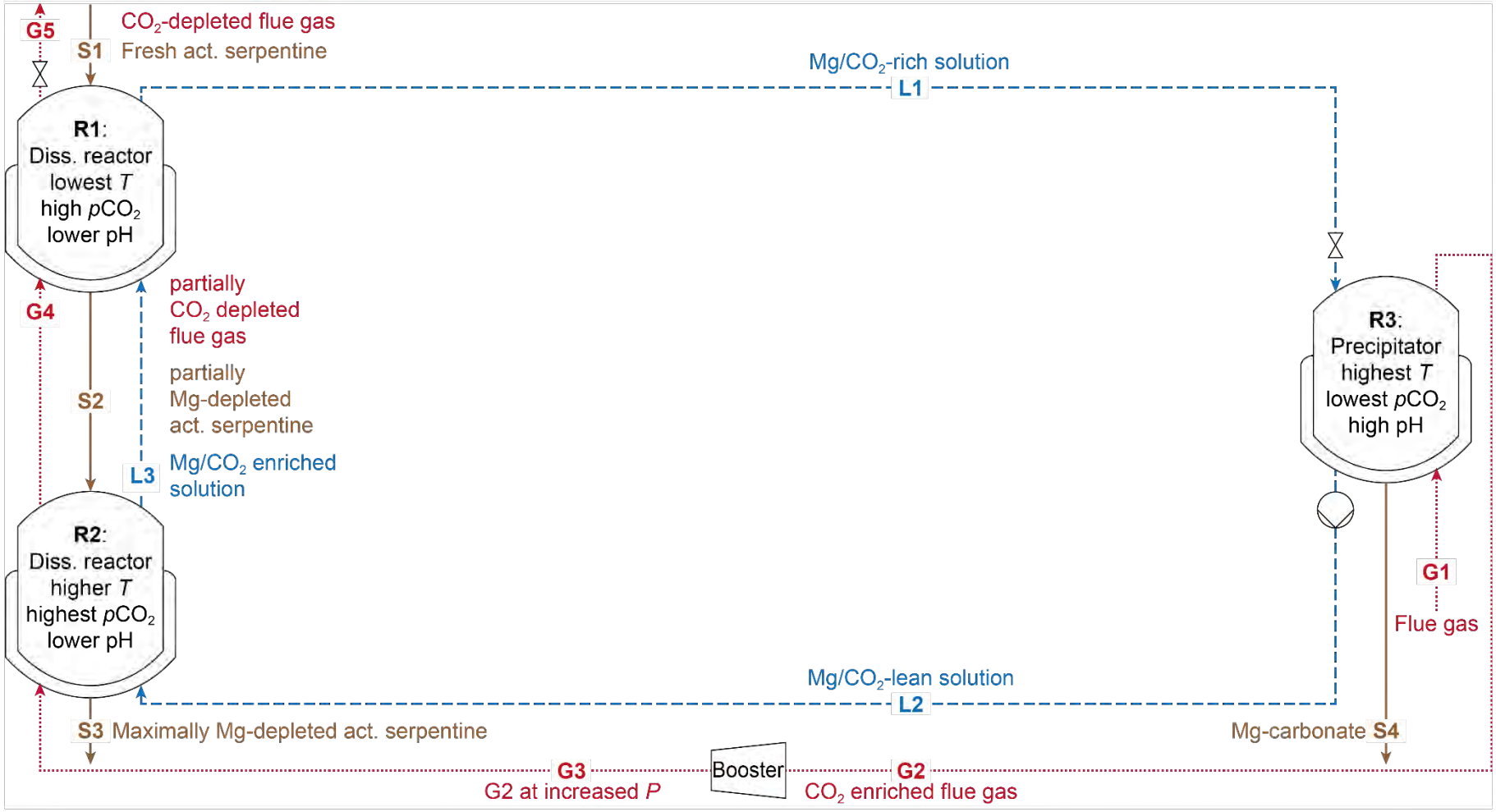


➡ Carbonation efficiency improved, but each strategy tackles only one of the two issues at the same time

Play ▶

Direct flue gas CO_2 mineralization – Carbonation

- A double-step process combining a **temperature swing** with a ***p*CO_2 swing**



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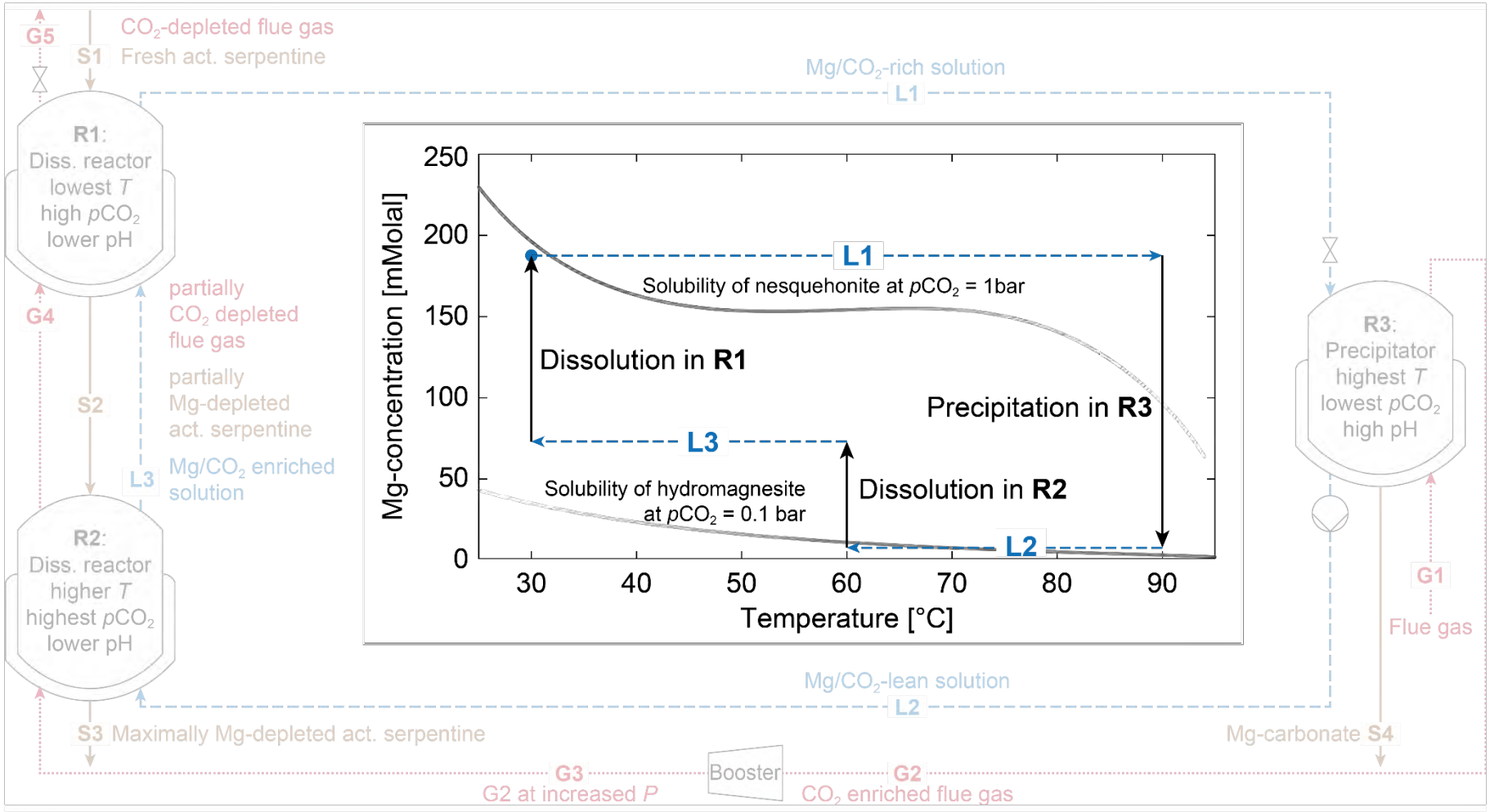

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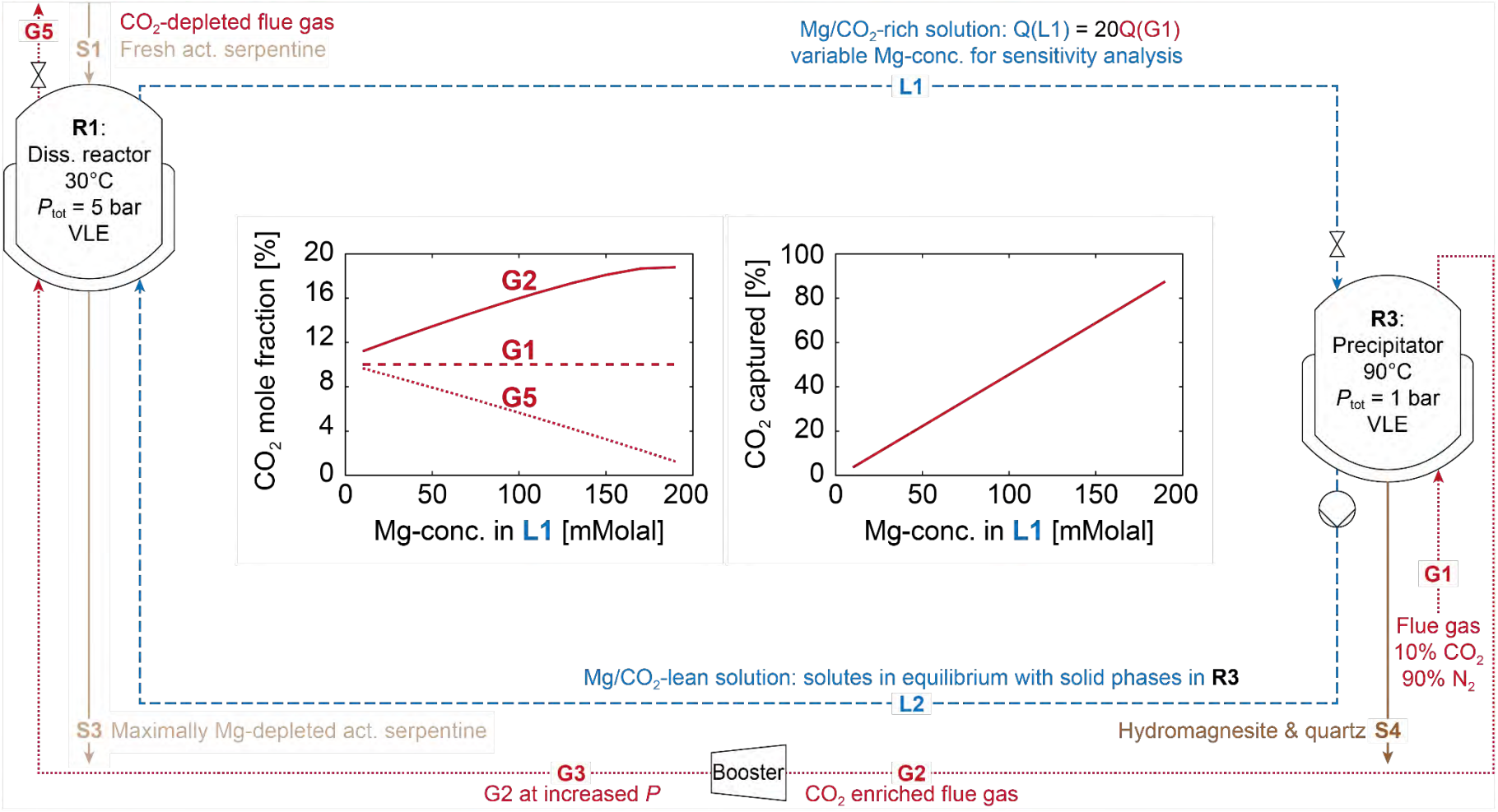
Direct flue gas CO_2 mineralization – Carbonation

- **Feasibility assessment** for the proposed *T*-*p*CO_2-swing process: **illustrative simulations**



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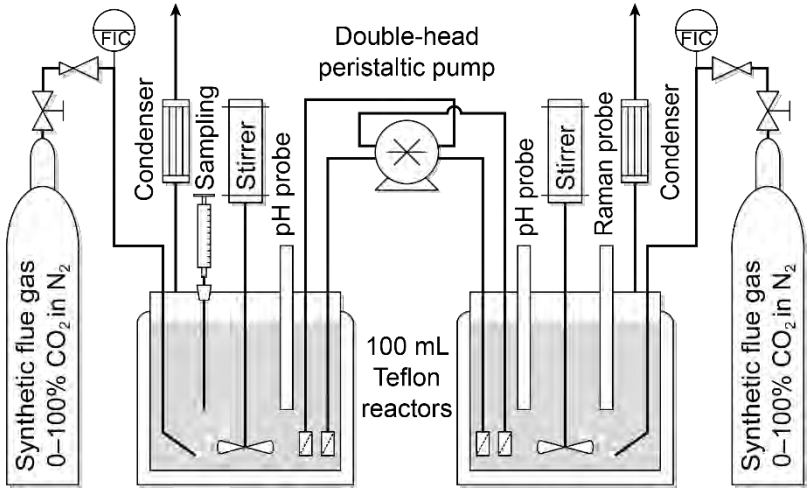
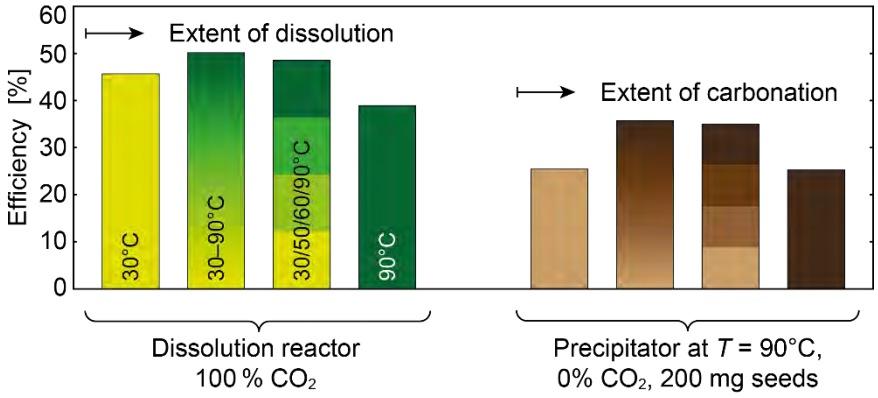
Direct flue gas CO_2 mineralization – Carbonation

- **Feasibility assessment** for the proposed *T*-*p*CO_2-swing process: **through experiments**

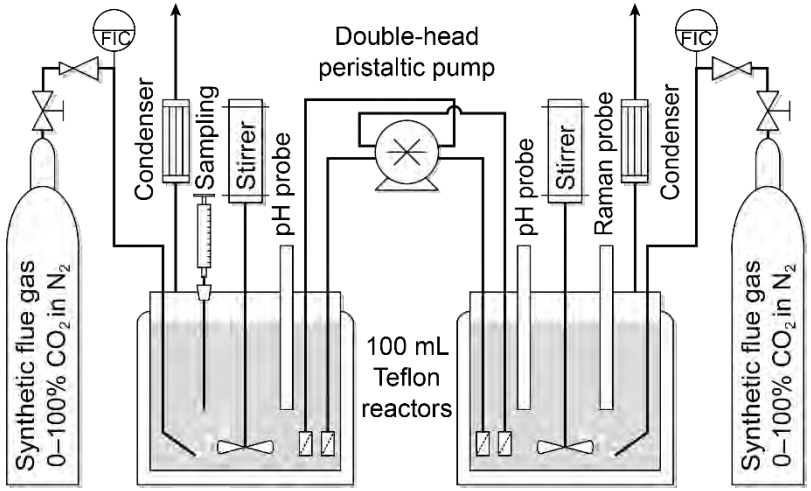


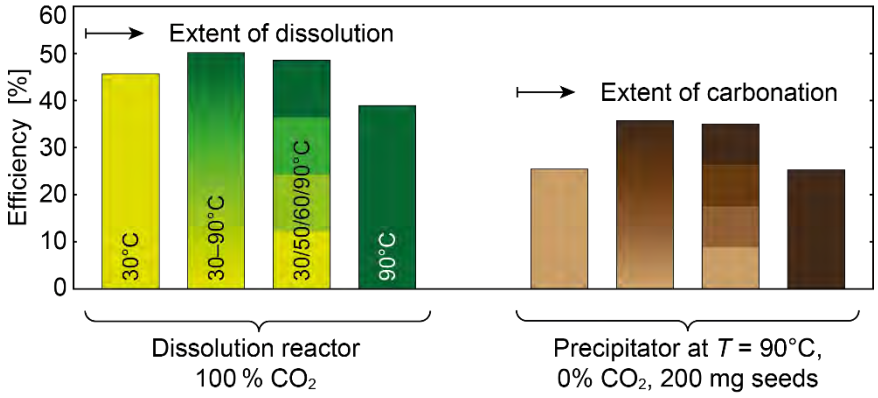


Werner et al., Phys Chem Chem Phys, submitted

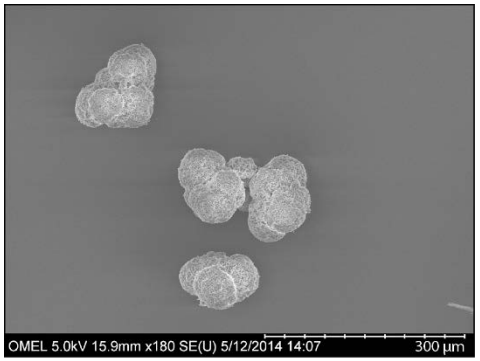
Direct flue gas CO_2 mineralization – Carbonation

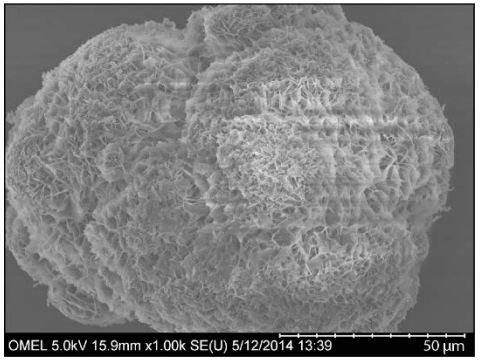
- Feasibility assessment for the proposed *T*-*p*CO_2-swing process: **double-step experiments**





- Pure Mg-carbonate product:





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Conclusions

- Thermal activation effective to promote serpentine reactivity
  - High extent of dissolution in less than **100 min**
  - Our model sheds light on corresp. dissolution mechanism and kinetics
- There is a route to the direct mineralization of flue gas CO_2
  - Activated serpentine can be carbonated under very lean operating conditions: **≤ 100°C** and **≤ 1 bar *p*CO_2**
  - The MgO-CO_2-H_2O systems allows to exploit a simple ***T*-swing** in combination with a ***p*CO_2 swing** for successful process design
  - Feasibility of this concept proven by simulations and through experiments
- Ultimate performance of the proposed route will be the outcome of a complex optimization process.

Back-ups

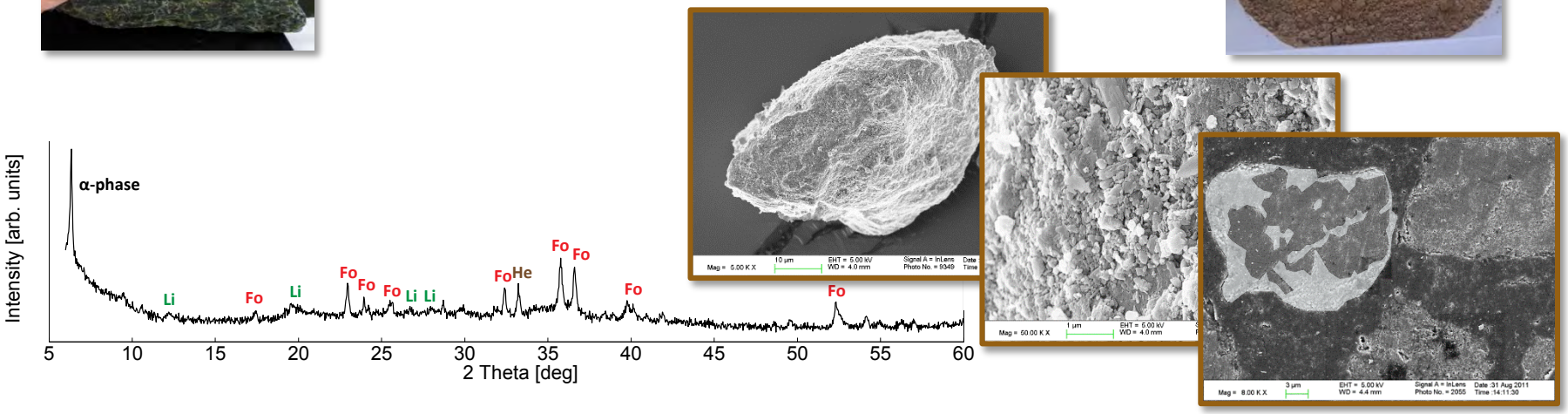
- Activation E-requirements
- Precipitation in the aS-CO_2-H_2O system
- Single-step carbonation
- Concurrent grinding
- Additional illustrative simulations
- Double-step carbonation

Direct flue gas CO_2 mineralization – Activation

- Capture integration should allow to **intensify the pretreatment** of precursor material

Mechanical & thermal activation of lizardite

$$Mg_3Si_2O_5(OH)_4 \longrightarrow Mg_3Si_2O_{6.5}(OH) + 1.5H_2O$$



particle size = -125 µm	**13 kWh/ton$_{sh}$**	-75 µm, lizardite serpentine (Gerdemann et al., 2001 Env Sci Tech)
heat activation @ T = 610°C	**206 kWh/ton$_{sh}$**	up to 630°C, c_p = 89 cal/mol/K, antigorite (King et al., 1967, RI6962)
dehydroxylation = 75%	**120 kWh/ton$_{sh}$**	100% dehydrox. (Govier and Arnold, 2004, ARC internal rep.)
	339 kWh/ton$_{sh}$ → **$$$/ton$_{sh}$**	Electricity as heat source, no heat integration (Gerdemann et al., 2001 Env Sci Tech)

Back-ups

Direct flue gas CO_2 mineralization – Activation

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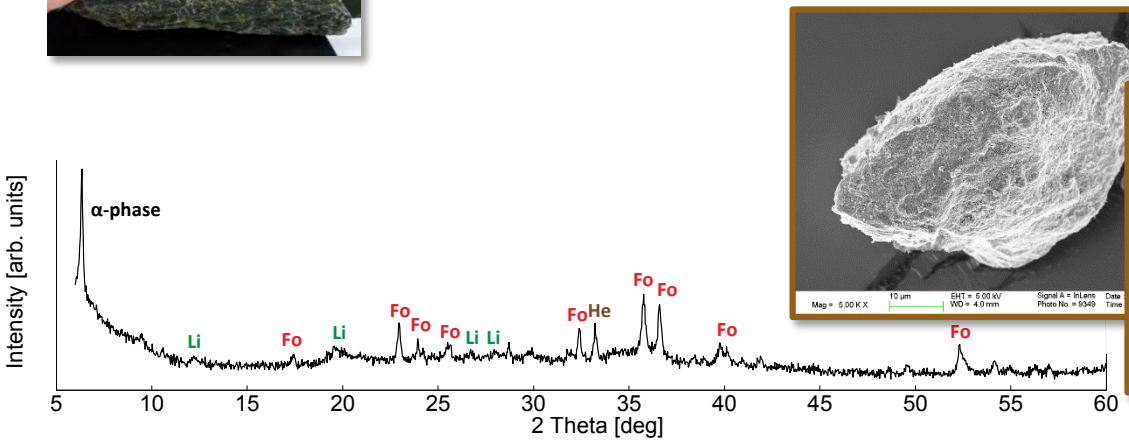

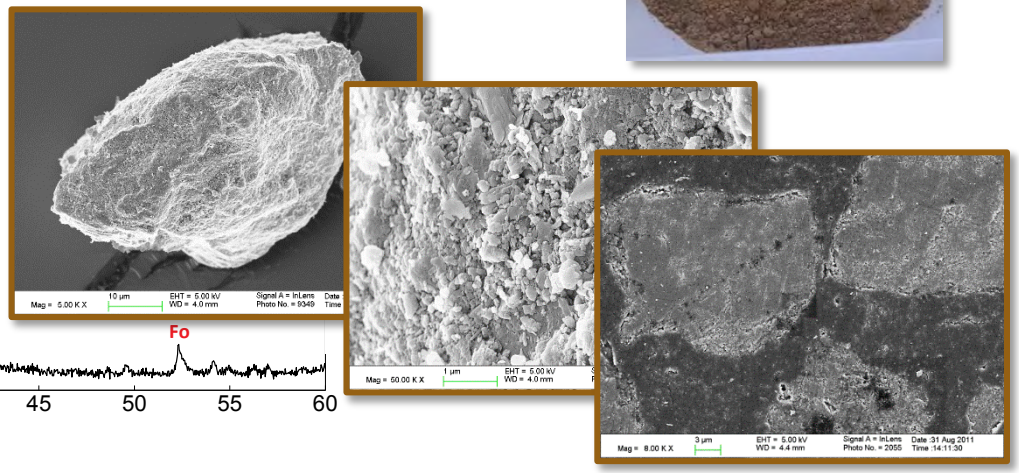

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heat activation @ T = 610°C — **206 kWh/ton$_{sh}$**

dehydroxylation = 75% — **120 kWh/ton$_{sh}$**

339 kWh/ton$_{sh}$

158 kWh/ton$_{sh}$ → **1.2 A$/ton$_{sh}$**

570 MJ/t, 80% heat recovered, 20% residual hydroxyls, Balucan et al., 2013, Int J GHG control

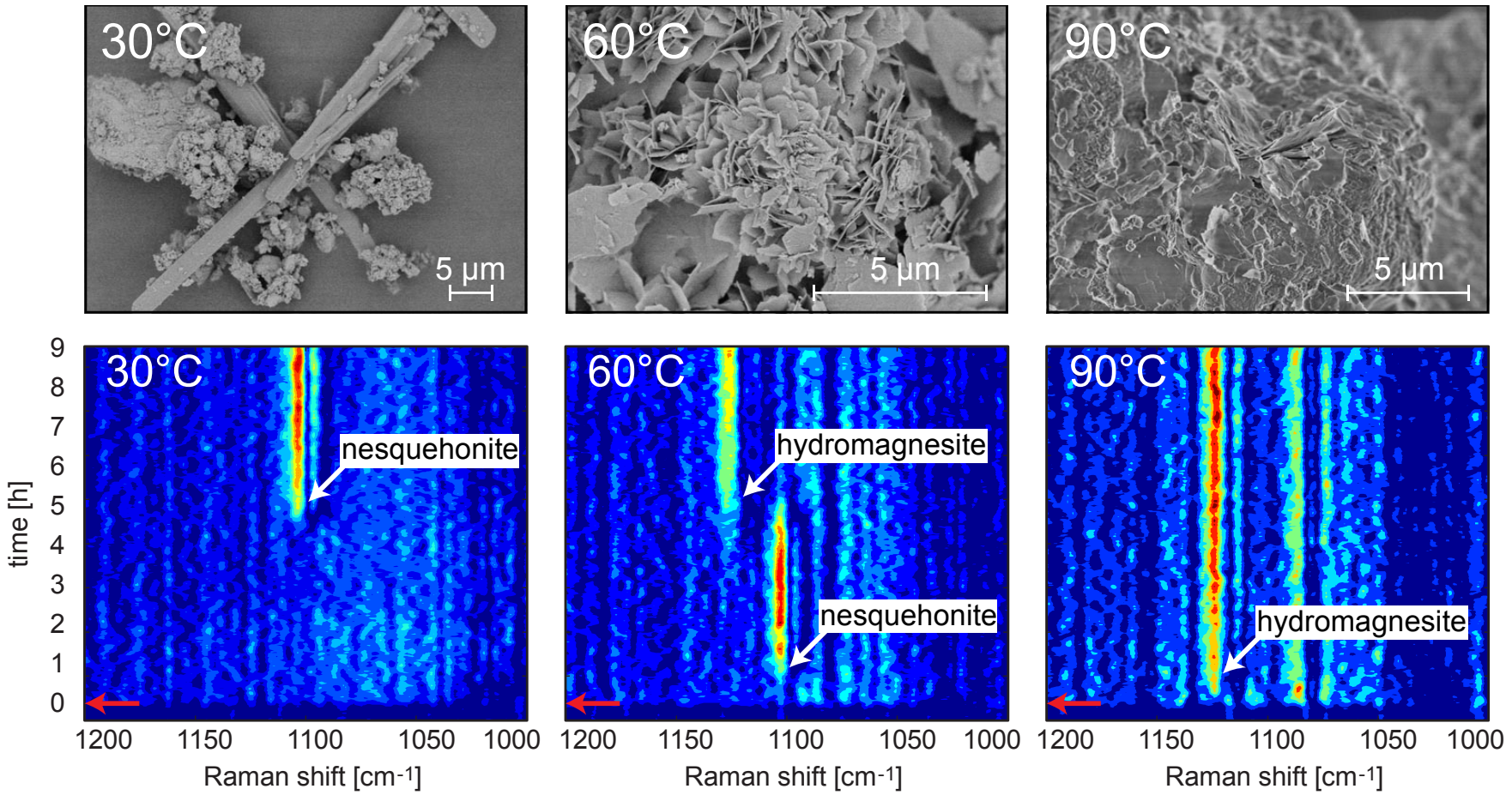
nat. gas as heat source, accounting for secondary emissions

Back-ups

Activated serpentine-CO_2-H_2O system

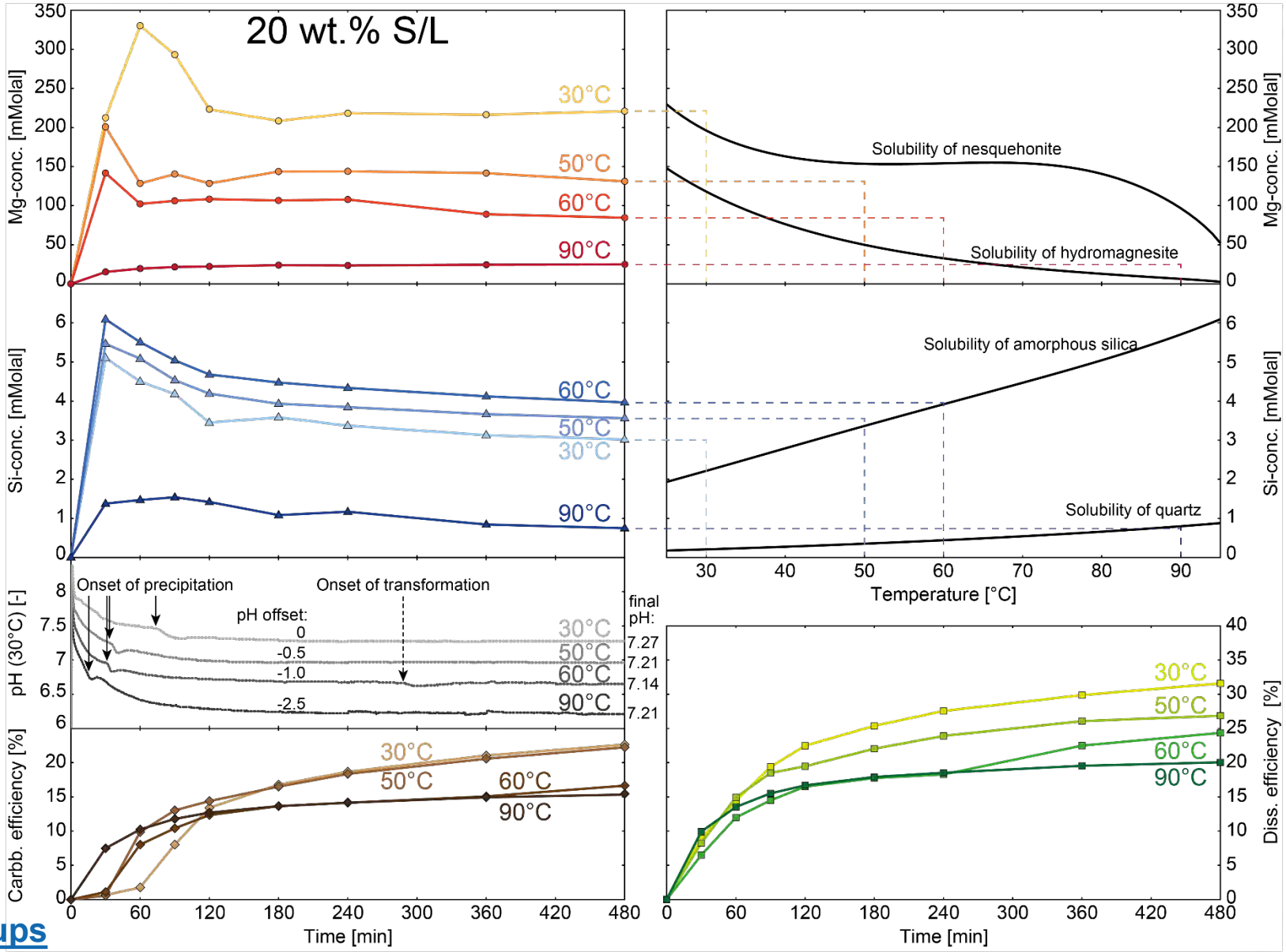
Mg-carbonate identification in product: SEM and Raman

- Conditions: S/L = 10% wt., pCO_2 = 1 bar, 10 h



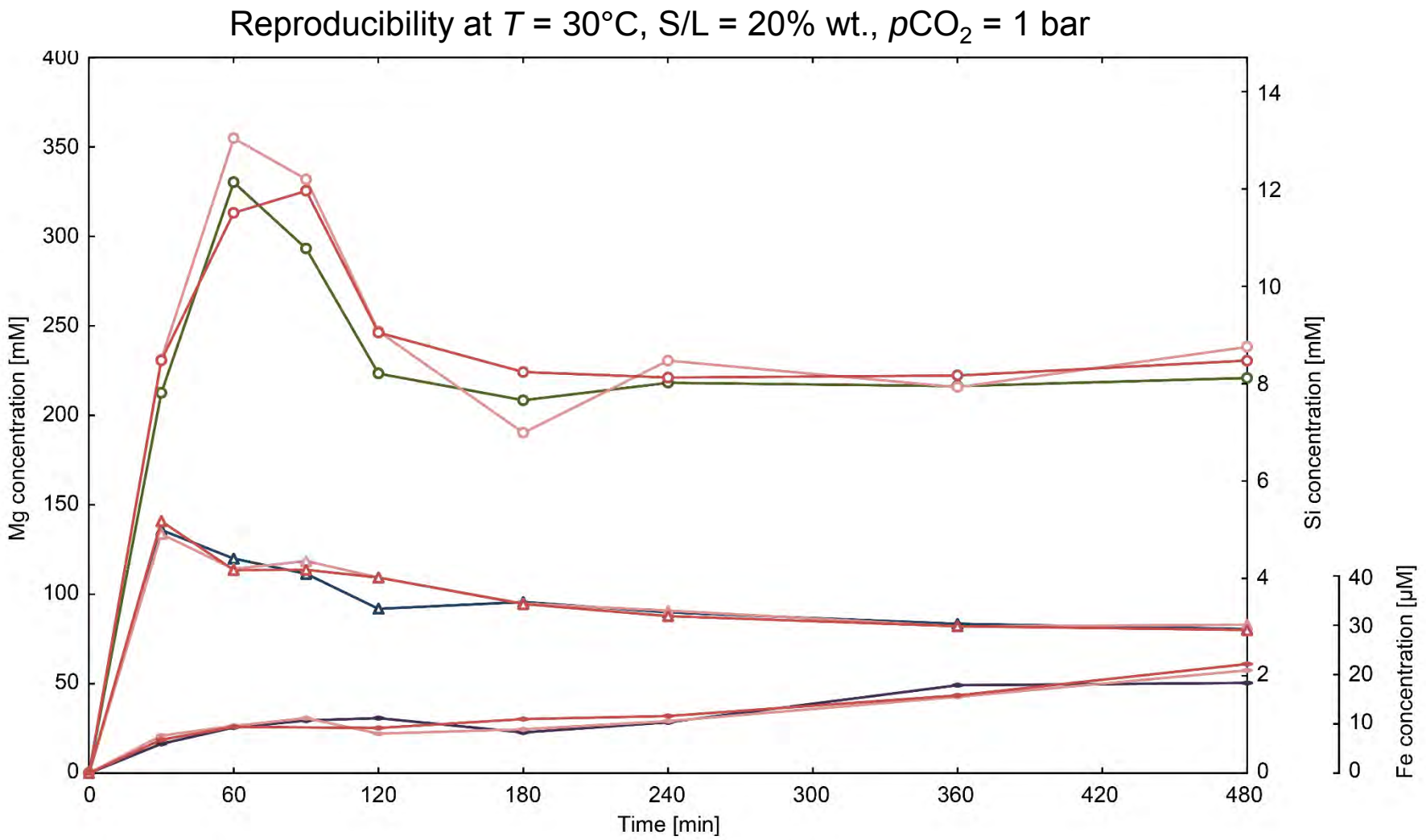
Back-ups

Parametric study on single-step carbonation



Back-ups

Single-step carbonation



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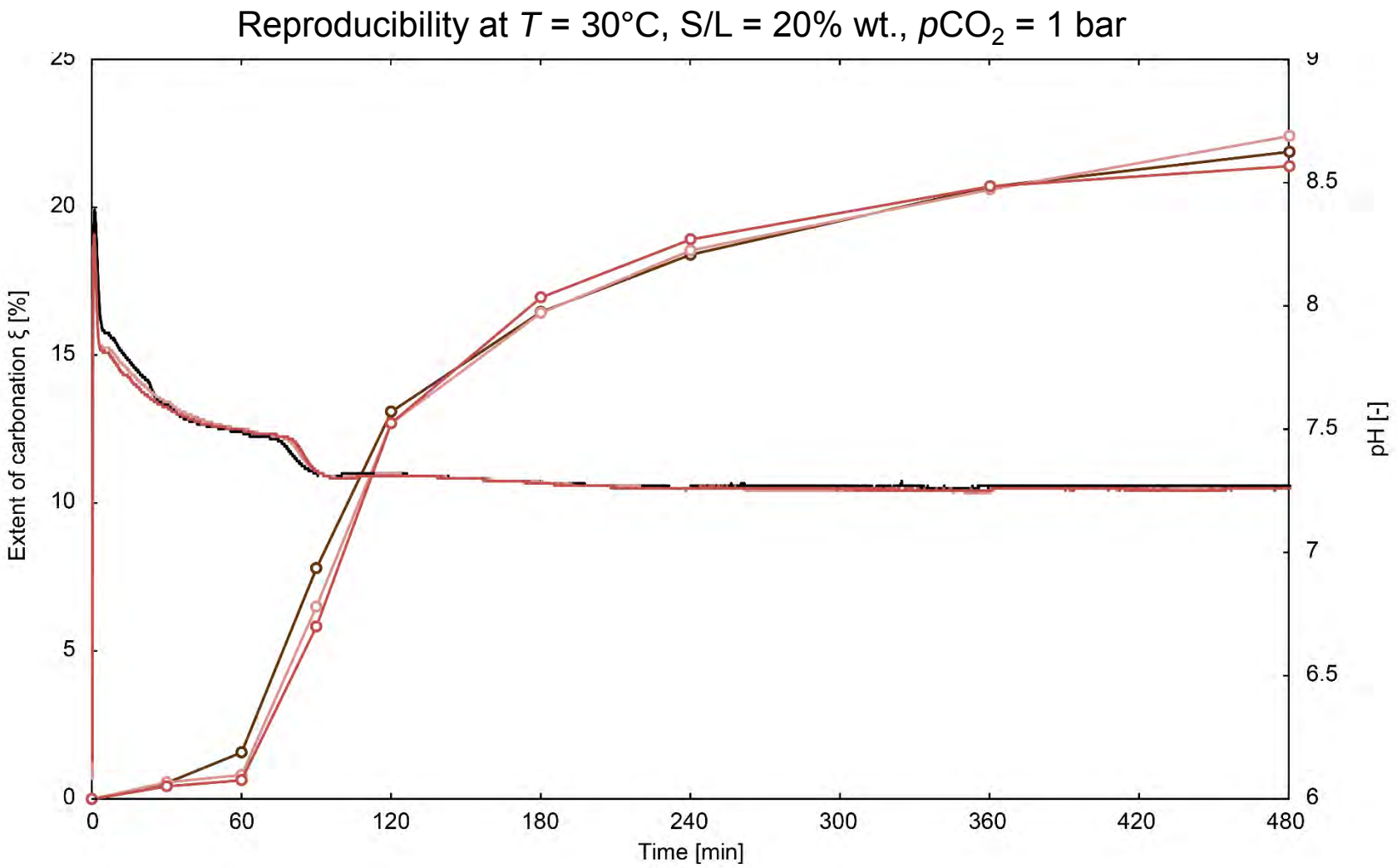
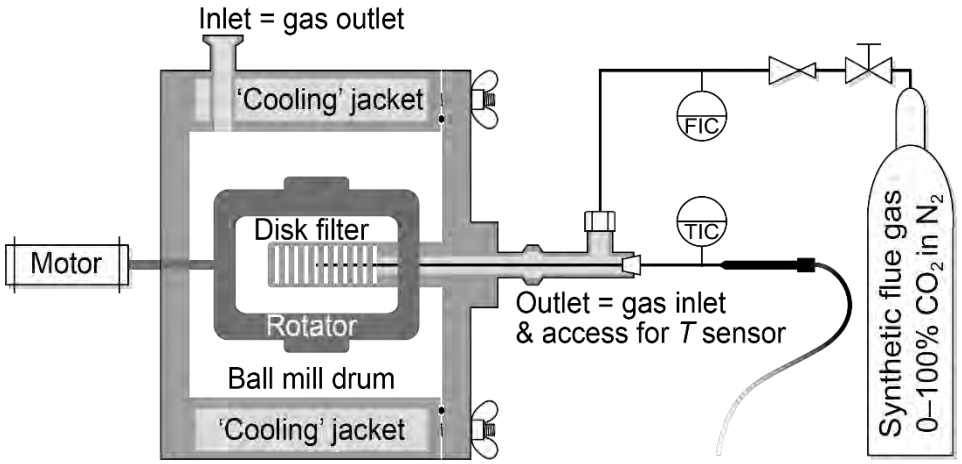
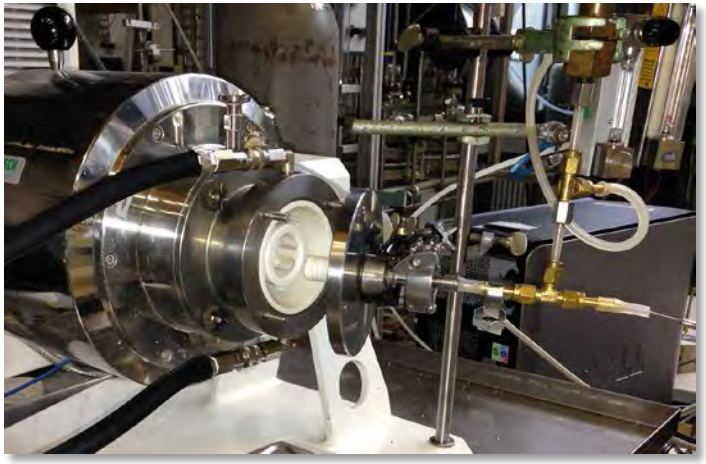


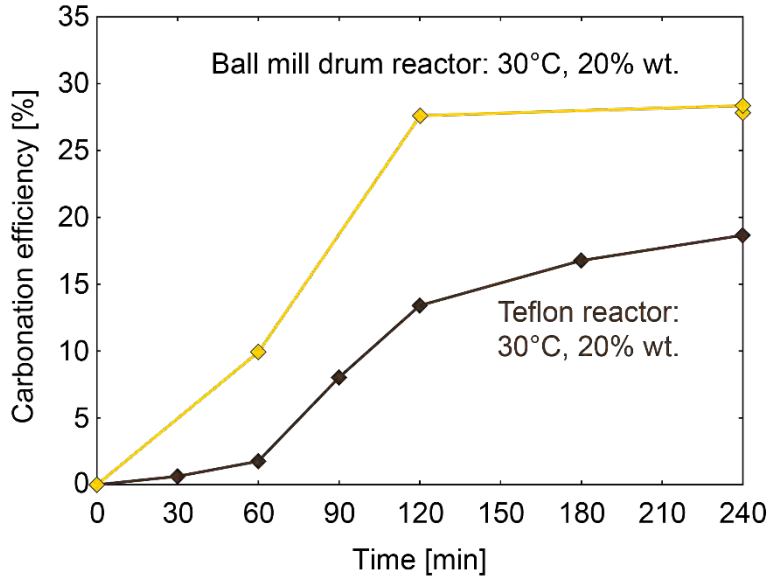
Back-ups

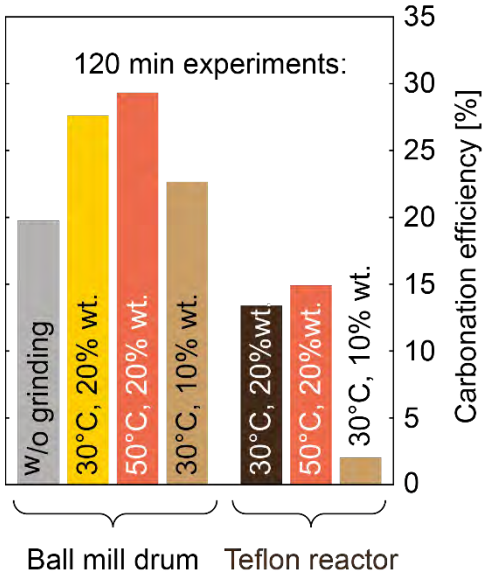
Single-step carbonation with concurrent grinding

- Upgrading a ball mill drum to yield 'reactor':





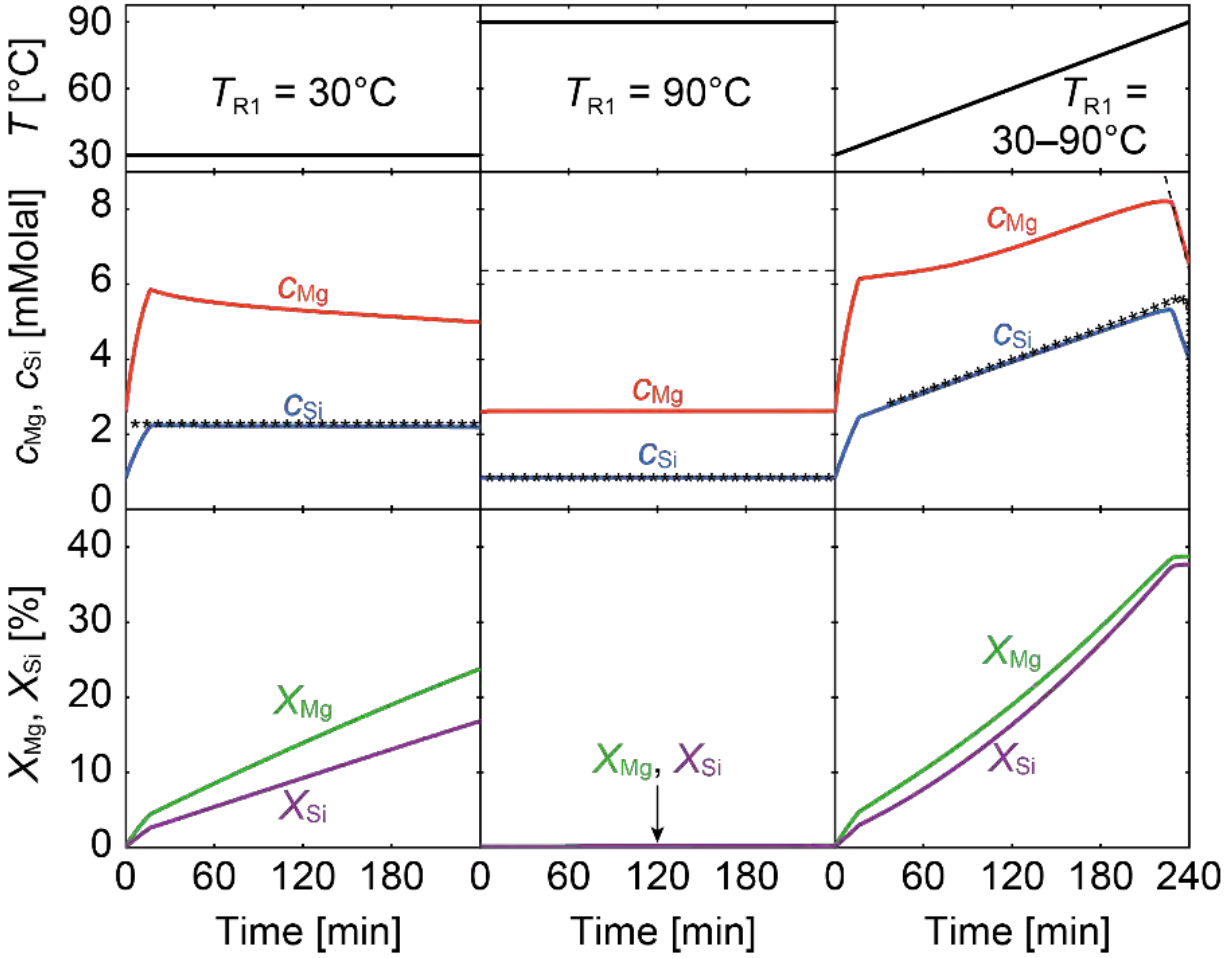




Back-ups

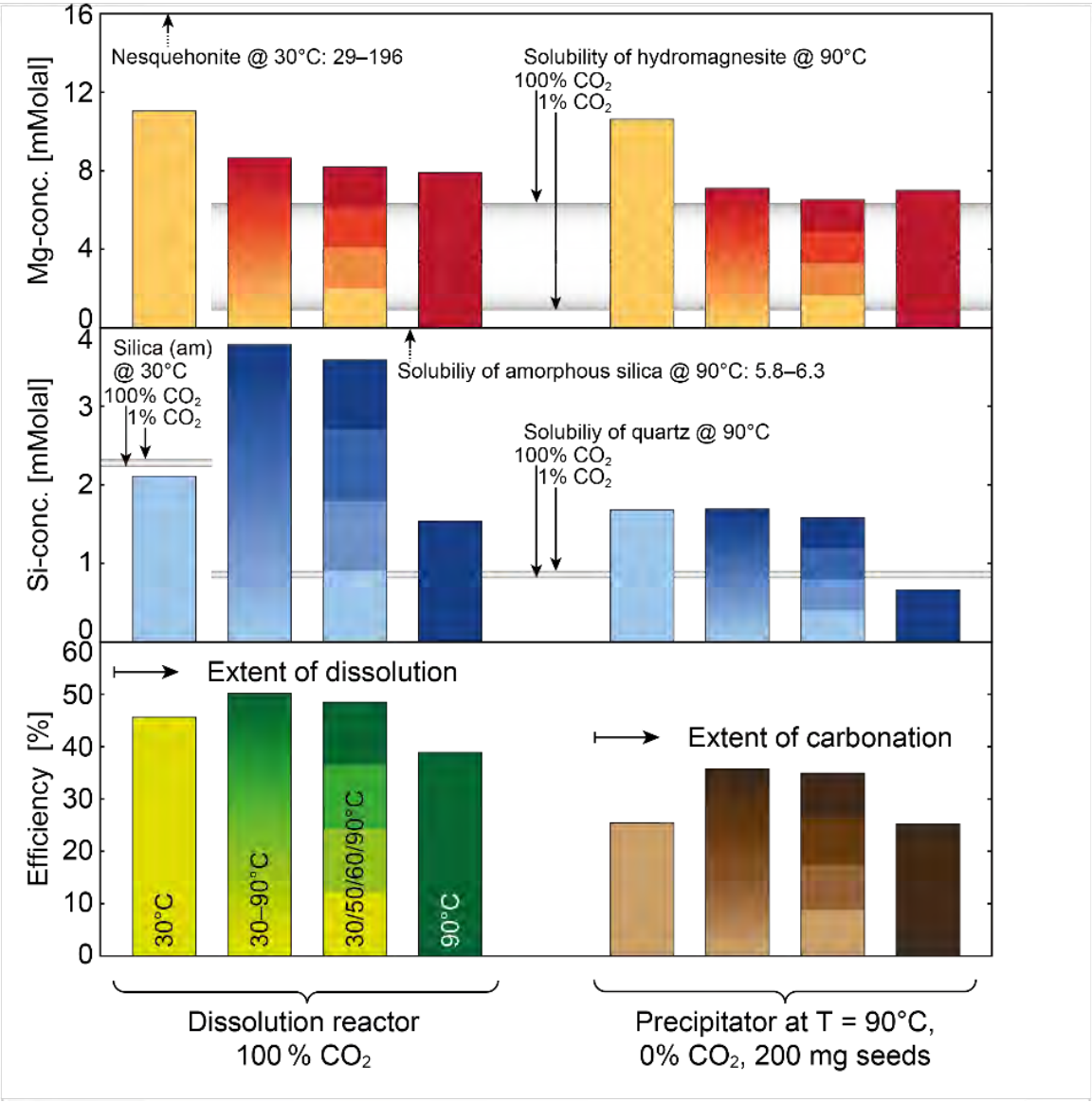
Additional illustrative simulations

- Dissolution of act. serpentine in R1 in flow through mode (f.f.eq. dissolution model used, no dissolution once solubility of Si-precipitate or Mg-carbonate reached)



Back-ups

Double-step carbonation



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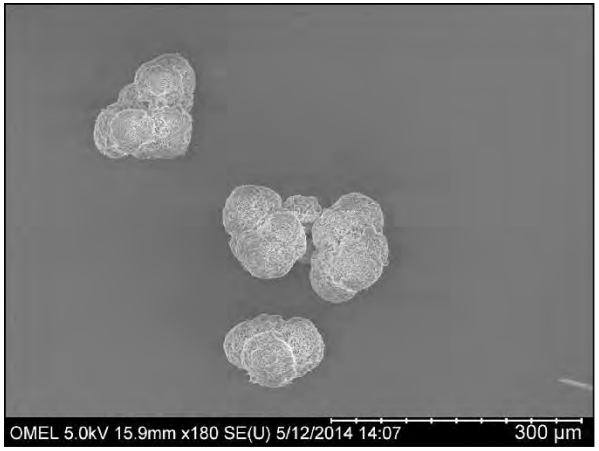

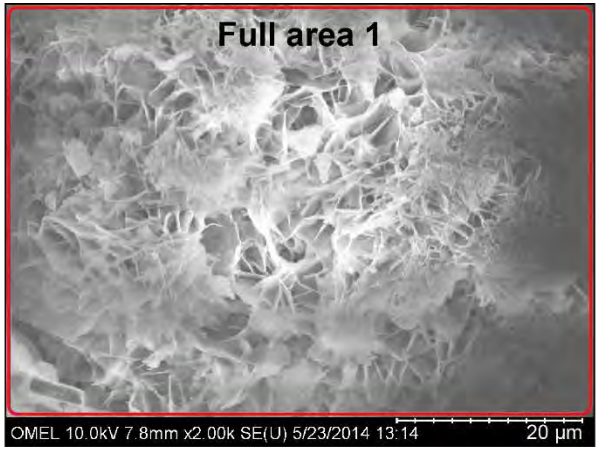

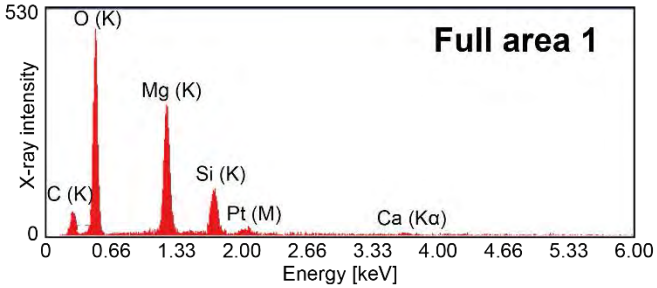

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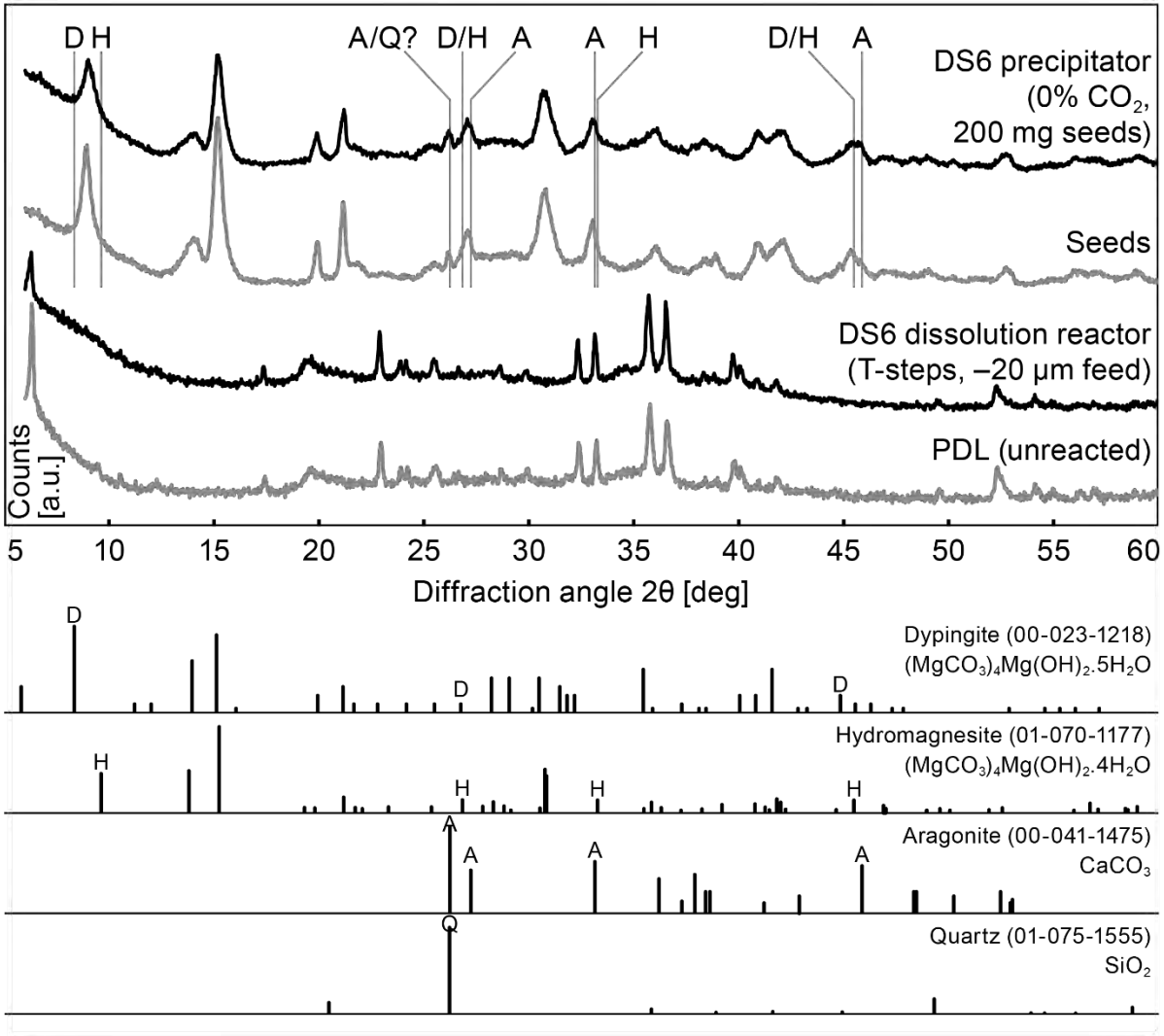

Back-ups

CO_2 mineralization

Natural process:

1. CO_2 dissolution and speciation:

$$CO_2(g) + H_2O \longrightarrow HCO_3^- + H^+$$

high pCO_2, low *T*

2. Cation extraction from Mg/Ca-rich source:

$$Mg_3Si_2O_5(OH)_4 + 6H^+ \longrightarrow 3Mg^{2+} + 2SiO_2 + 5H_2O$$

low pH, high *T*

3. Carbonate precipitation:

$$Mg^{2+} + 2HCO_3^- \longrightarrow MgCO_3 + CO_2 + H_2O$$

high pH, high *T*

Industrial application:

- Enabling **utilization** (added-value) and **permanent storage** (CO_2 mitigation)

CO_2 mineralization

Natural process:

1. CO_2 dissolution and speciation:

$$CO_2(g) + H_2O \longrightarrow HCO_3^- + H^+$$

preliminary capture step — high pCO_2, low T

2. Cation extraction from Mg/Ca-rich source:

$$Mg_3Si_2O_5(OH)_4 + 6H^+ \longrightarrow 3Mg^{2+} + 2SiO_2 + 5H_2O$$

feed activation — low pH, high T

3. Carbonate precipitation:

$$Mg^{2+} + 2HCO_3^- \longrightarrow MgCO_3 + CO_2 + H_2O$$

additives (recoverable) — high pH, high T

Industrial application:

- Enabling **utilization** (added-value) and **permanent storage** (CO_2 mitigation)

CO_2 mineralization with capture integration

Natural process:

1. CO_2 dissolution and speciation:

$$CO_2(g) + H_2O \longrightarrow HCO_3^- + H^+$$

capture integration → low pCO_2, low *T*

2. Cation extraction from Mg/Ca-rich source:

$$Mg_3Si_2O_5(OH)_4 + 6H^+ \longrightarrow 3Mg^{2+} + 2SiO_2 + 5H_2O$$

feed activation → low pH, high *T*

3. Carbonate precipitation:

$$Mg^{2+} + 2HCO_3^- \longrightarrow MgCO_3 + CO_2 + H_2O$$

additives (recoverable) → high pH, high *T*

Industrial application:

- Enabling **utilization** (added-value) and **permanent storage** (CO_2 mitigation)
- **Capture integration** permits intensification of feed activation or use of pH-tuning additives