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Dissolution and carbonation of activated serpentine for combined capture and storage

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TCCS-6

Accelerated Carbonation for Environmental and Materials Engineering

Trondheim, Norway, 14 – 16 June 2011

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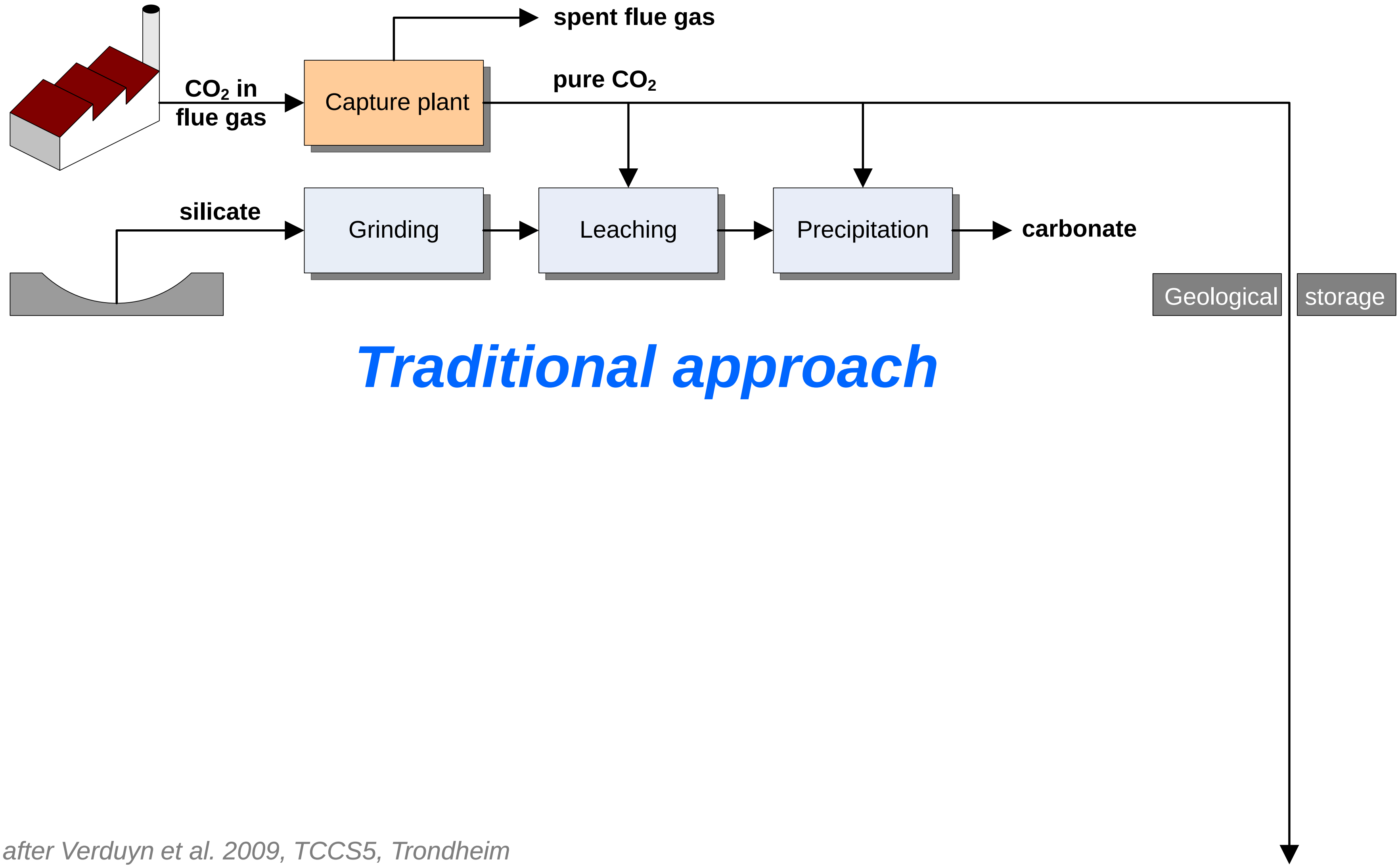
2) University of Rome, Thor Vergata

Outline

- Flue gas mineralization – the concept
- Experimental setup and material
- Capture via mineralization:
  - EQ3/6 equilibrium simulations
  - Dissolution experiments
  - Dissolution model
- Storage via mineralization:
  - EQ3/6 equilibrium simulations

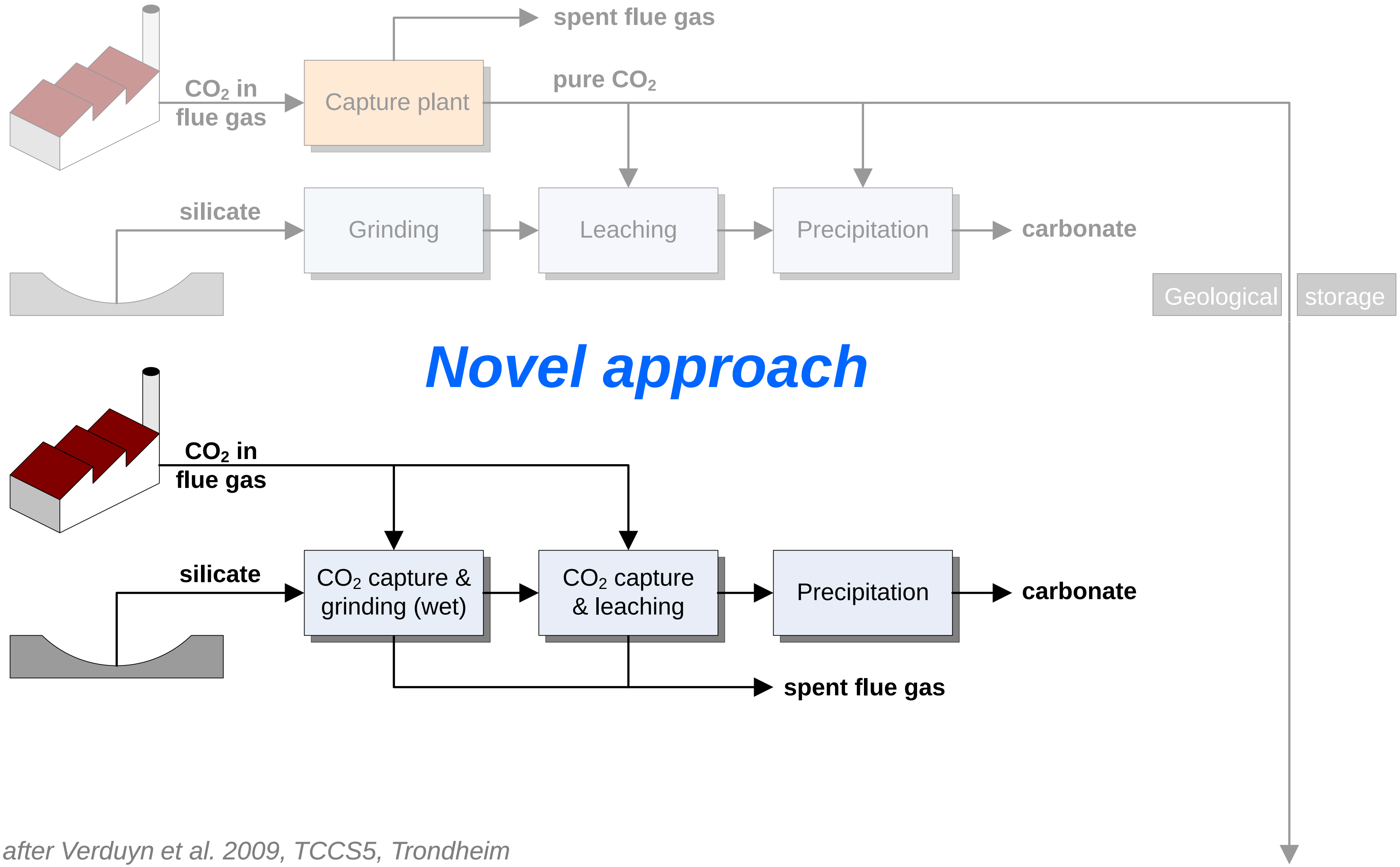
Flue gas mineralization within a CCS system



Traditional approach

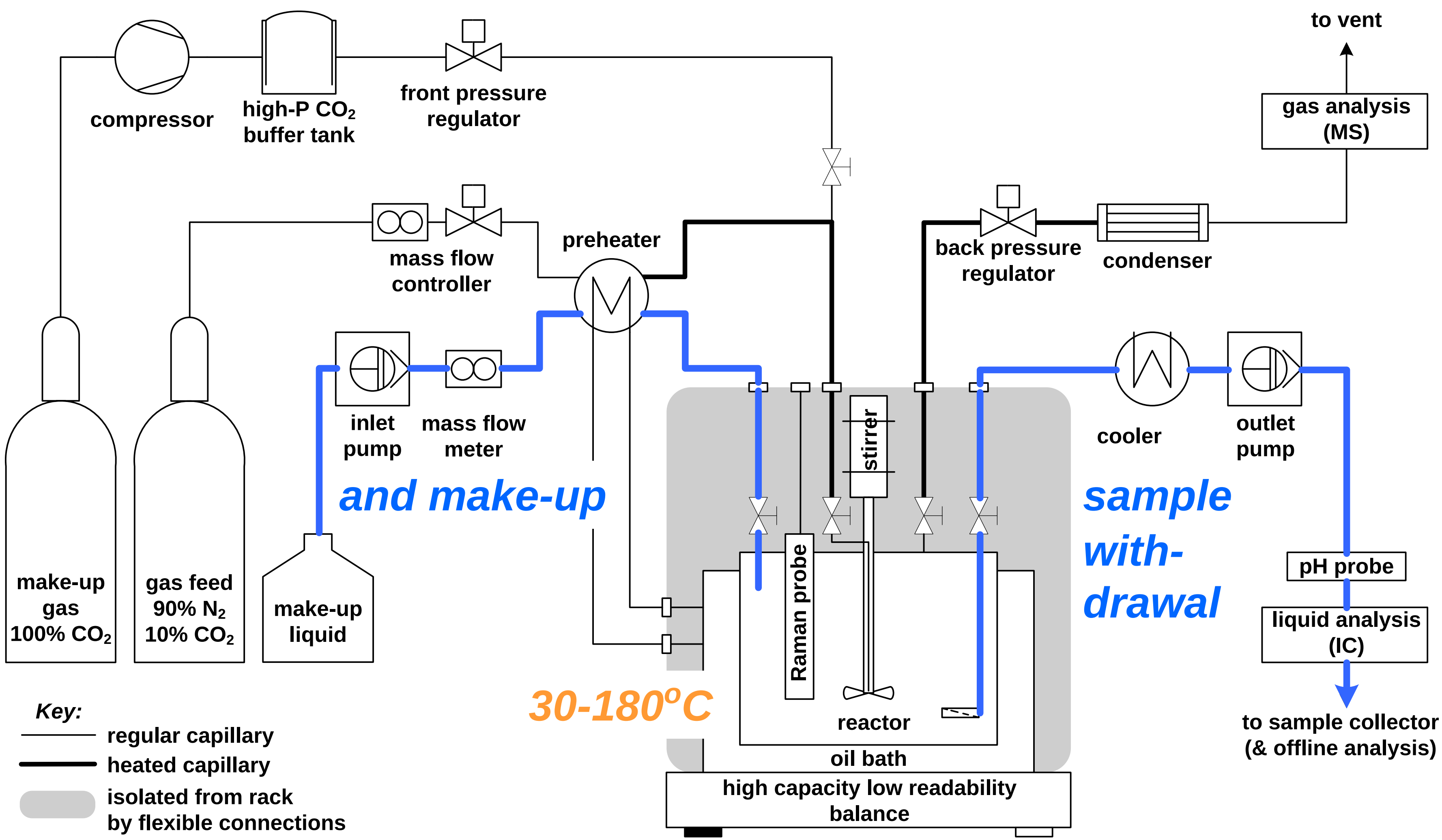
after Verduyn et al. 2009, TCCS5, Trondheim

Flue gas mineralization within a CCS system

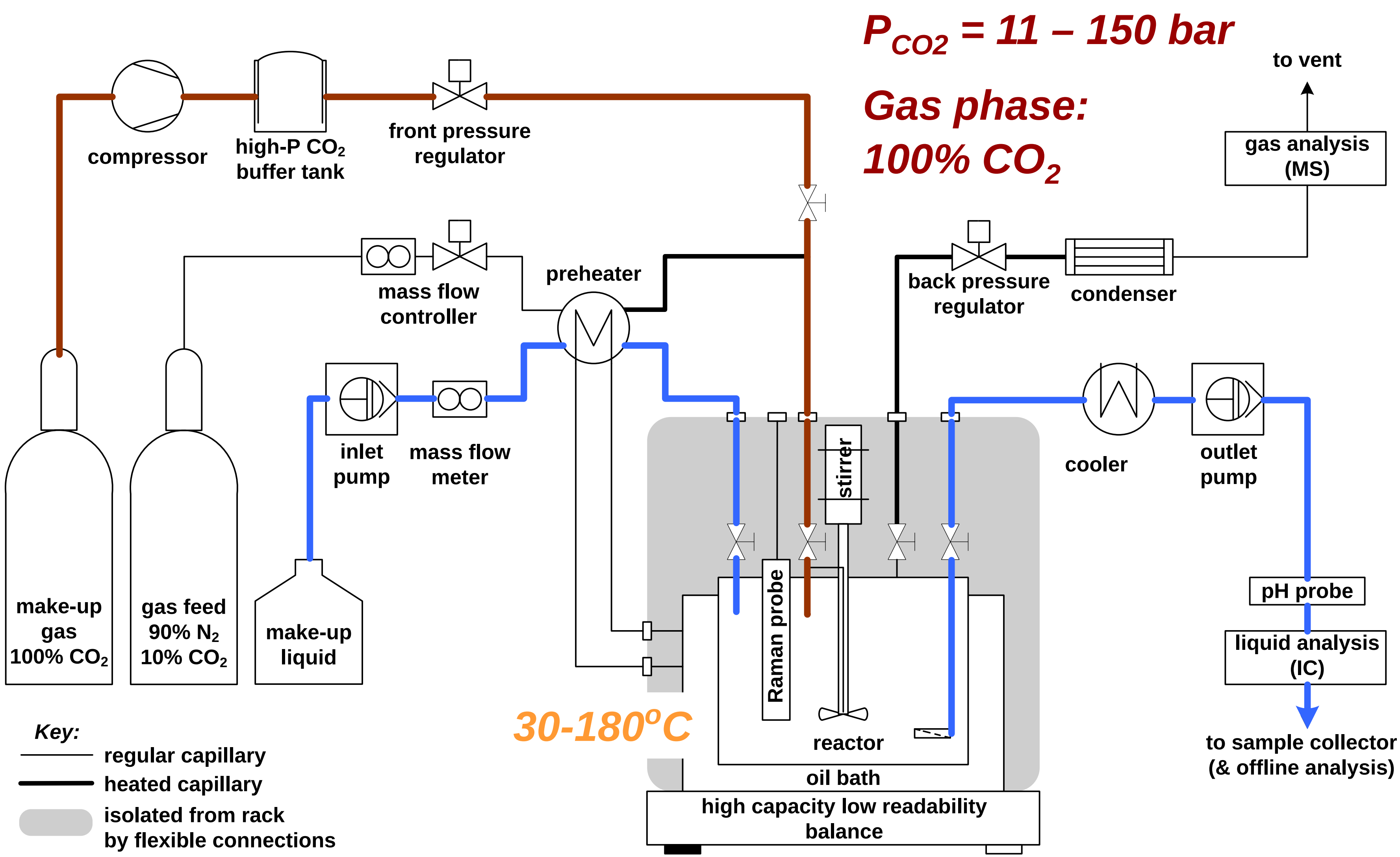


after Verduyn et al. 2009, TCCS5, Trondheim

Mineralization plant



Mineralization plant



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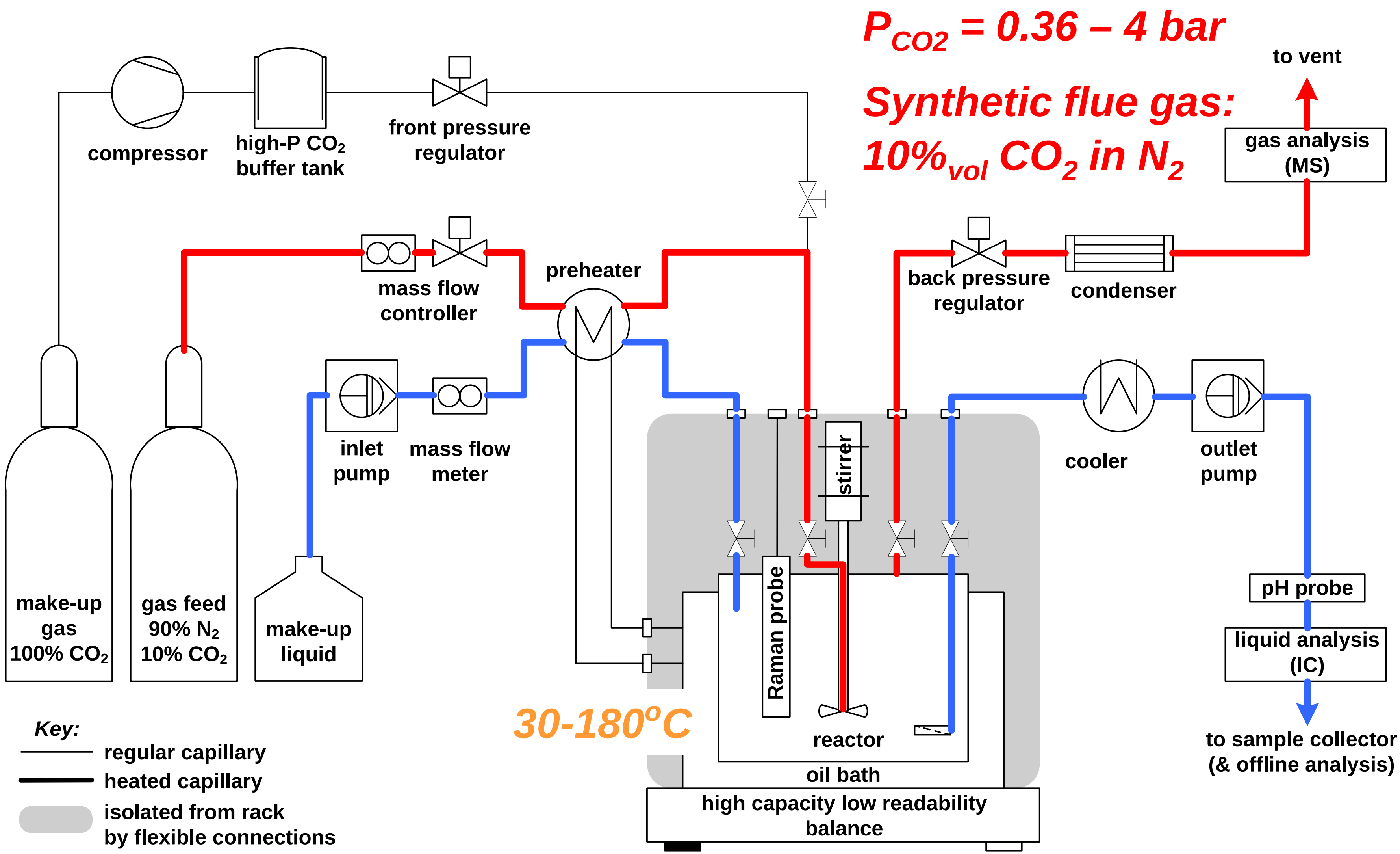
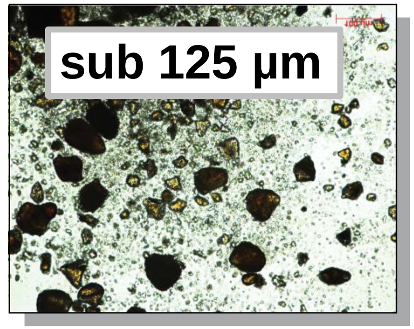
Mineralization plant

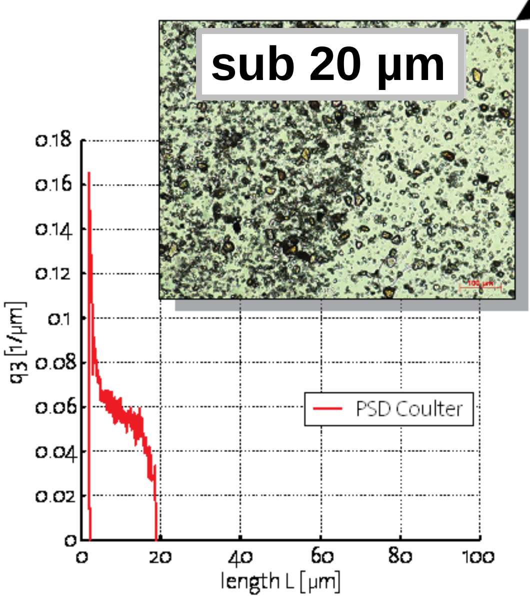


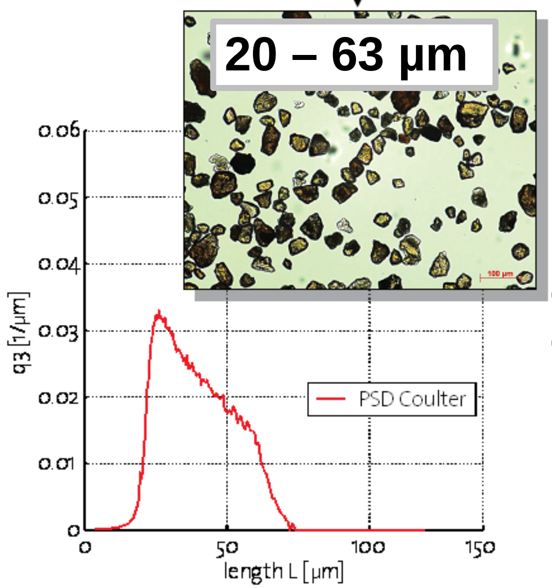
Activated serpentine

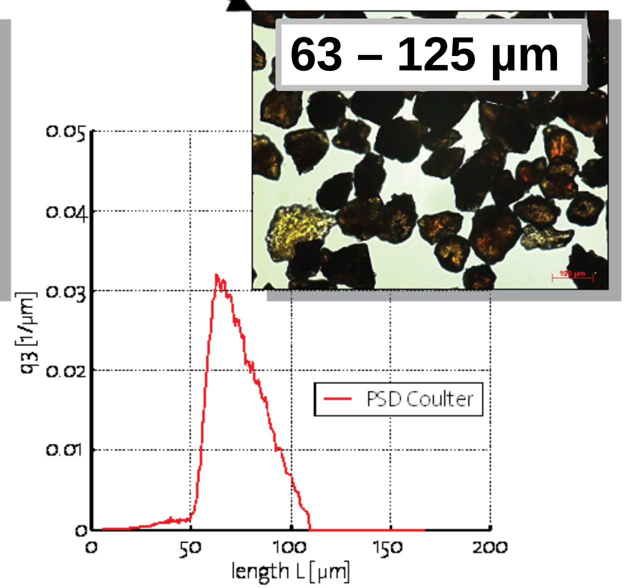
- $Mg_{2.42}Fe_{0.58}Si_2O_5(OH)_4$
- dry ground to <125 µm
- thermal activation at 600° C
- 1.5 mol H_2O per mole serpentine removed



- fractionation by dry sieving
- fines removal w/ EtOH
- micropores (2-3 nm) measured (BET method)



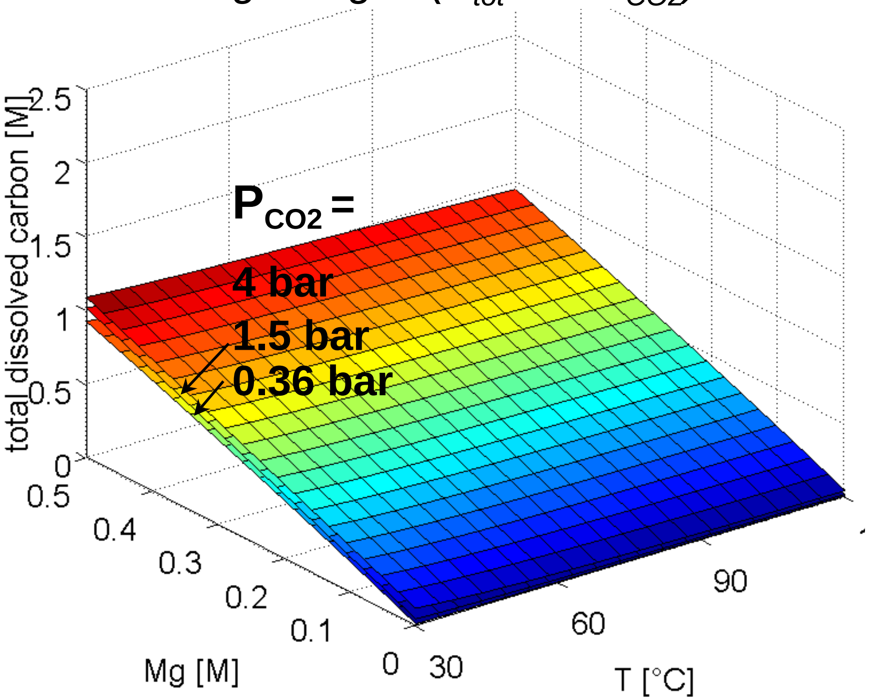




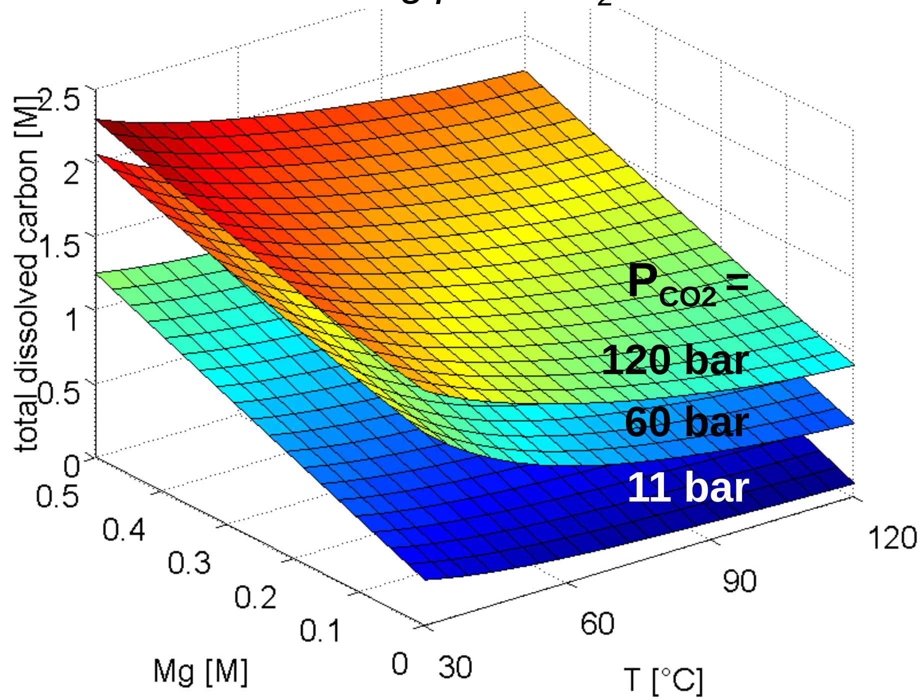
Capture part: EQ3/6 equilibrium simulations

CO_2 solubility as function of T and $[Mg^{2+}]$, at different P_{CO2} levels

using flue gas ($P_{tot} = 10P_{CO2}$):



using pure CO_2:



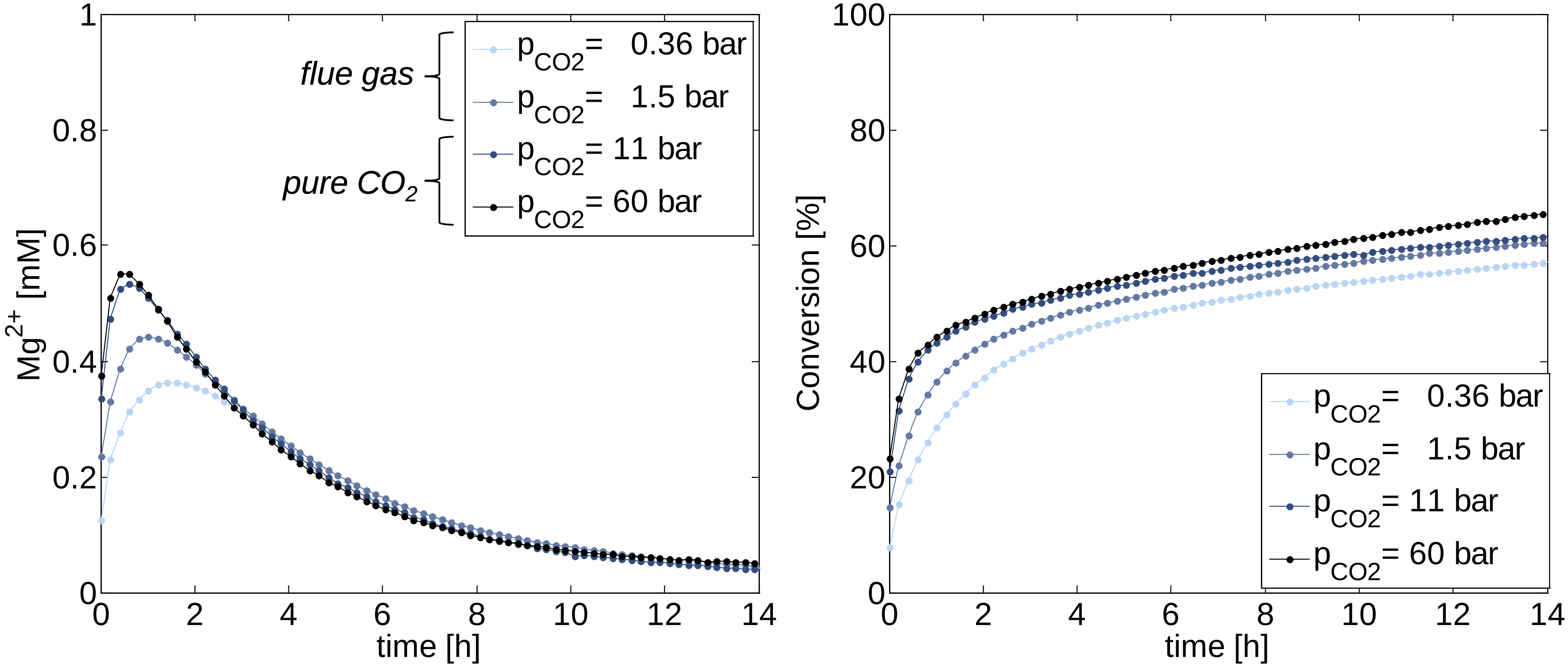
- If flue gas used: CO_2 solubility predominately sensitive to $[Mg^{2+}]$
- If pure CO_2 used: low T favorable, highest P_{CO2} not worth the while

→ even at low P_{CO2} high CO_2 loads possible

Act. serpentine dissolution experiments

$Mg_{2.42}$ $Fe_{0.58}Si_2O_5(OH)_4$

Magnesium concentration and conversion at 30°C:

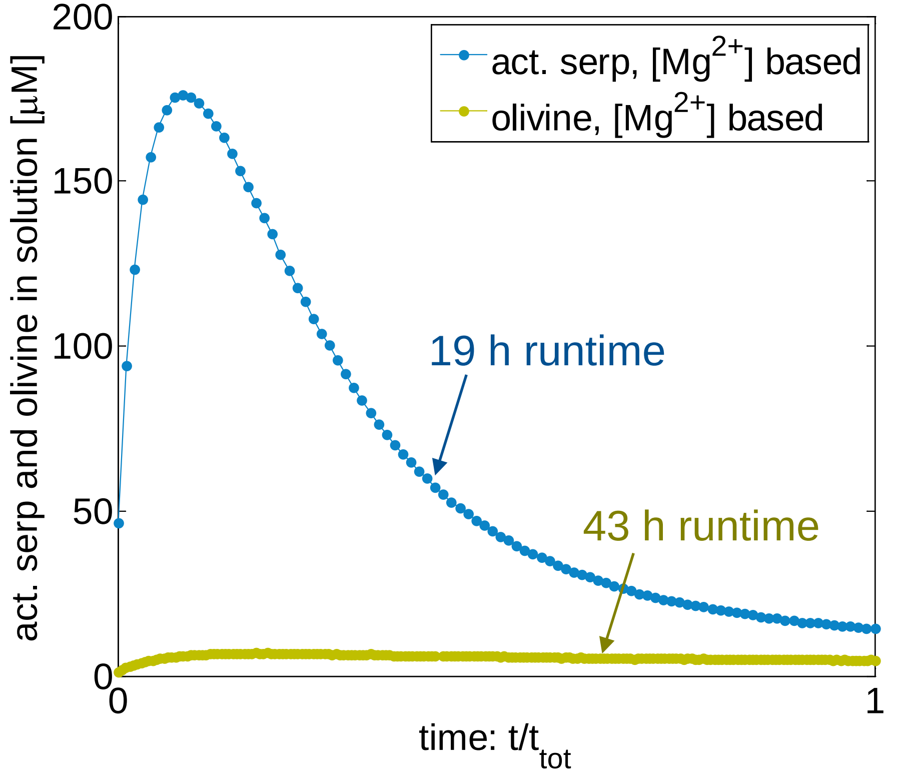


→ Dissolution using flue gas similarly effective as with pure CO_2

→ Complex dissoltuion mechanism: Drastic slowdown after fast initial phase

Olivine vs activated serpentine dissolution

T = 30°C, P_{CO2} = 0.36 bar, flue gas mode, 20-63 µm fraction



→ Olivine so far "best candidate" Mg-silicate (most reactive)*

**e.g. O'Connor et al,. 2005, Albany Research Center*

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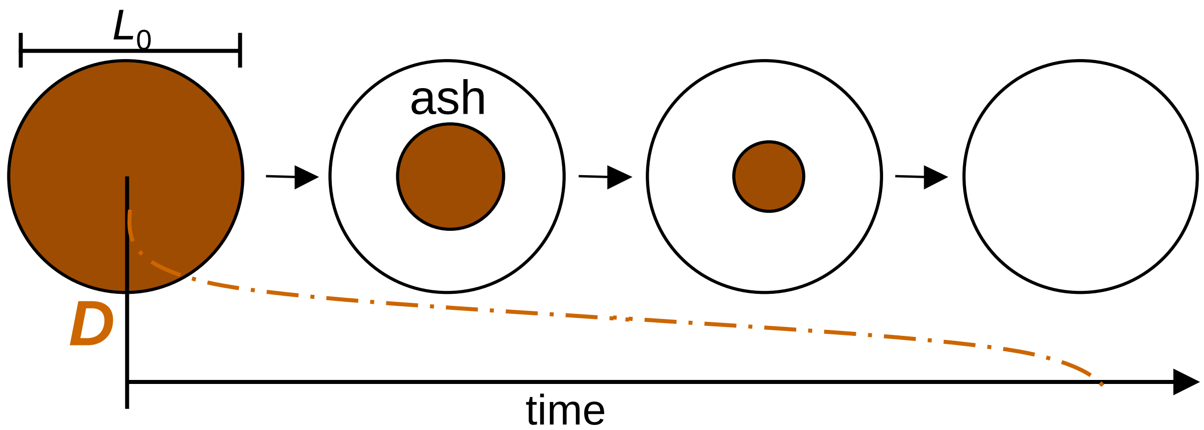
Dissolution model for natural serpentine

Natural serpentine dissolves acc. to **Shrinking core** model*

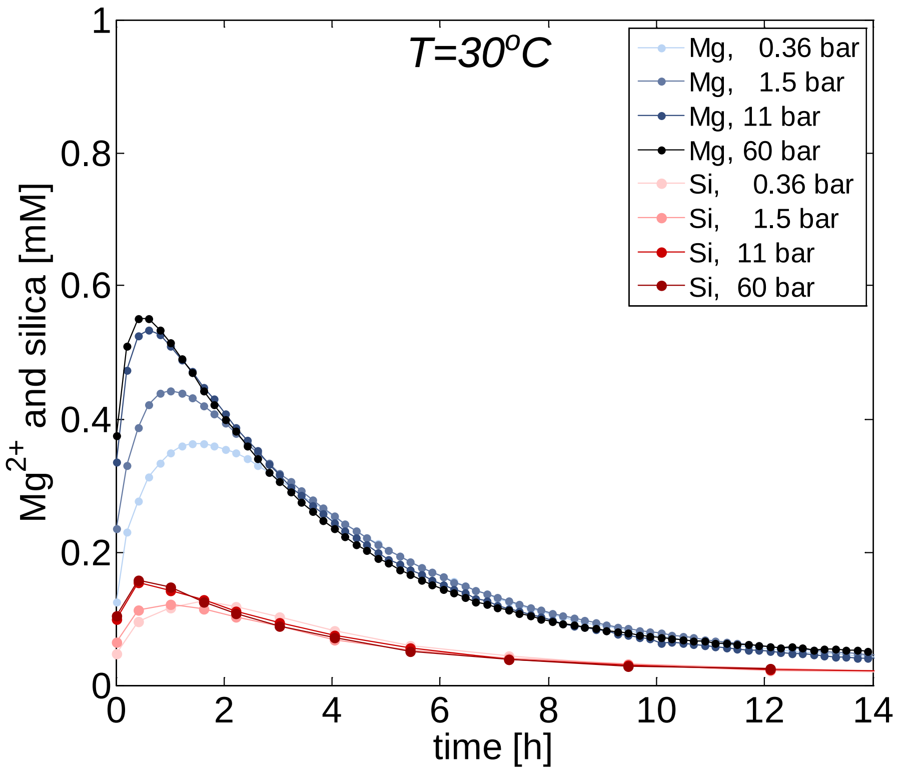


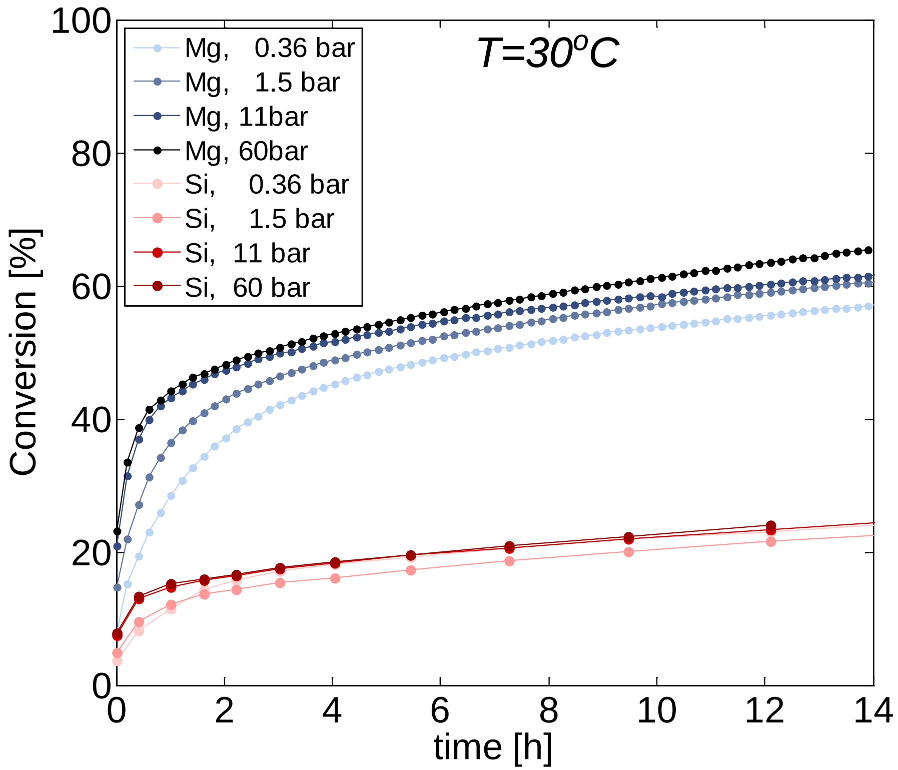
- Population balance: $$\frac{\partial n}{\partial t} - \frac{\partial Dn}{\partial L} = 0$$ n = particle population, PSD
  D = dL/dt, dissolution rate
- Dissolution rate: $$D = f\left(L, L_0\right)$$ not constant, diffusion controls
- Solute mass balance: $$V\frac{dc}{dt} = \frac{dm}{dt} - Qc$$ c = solute concentration
  m = mass of particle population

**e.g. Teir et al., 2007, Int J Miner Process 83;*
Van Essendelft et al., 2009/2010, Ind Eng Chem Res 48/49

Dissolution model for activated serpentine

- Presence of micropores and altered crystal structure cause complex, incongruent dissolution behavior
- $Mg_{2.42}Fe_{0.58}Si_2O_5(OH)_4$ → **Silica** detected in reactor solution:





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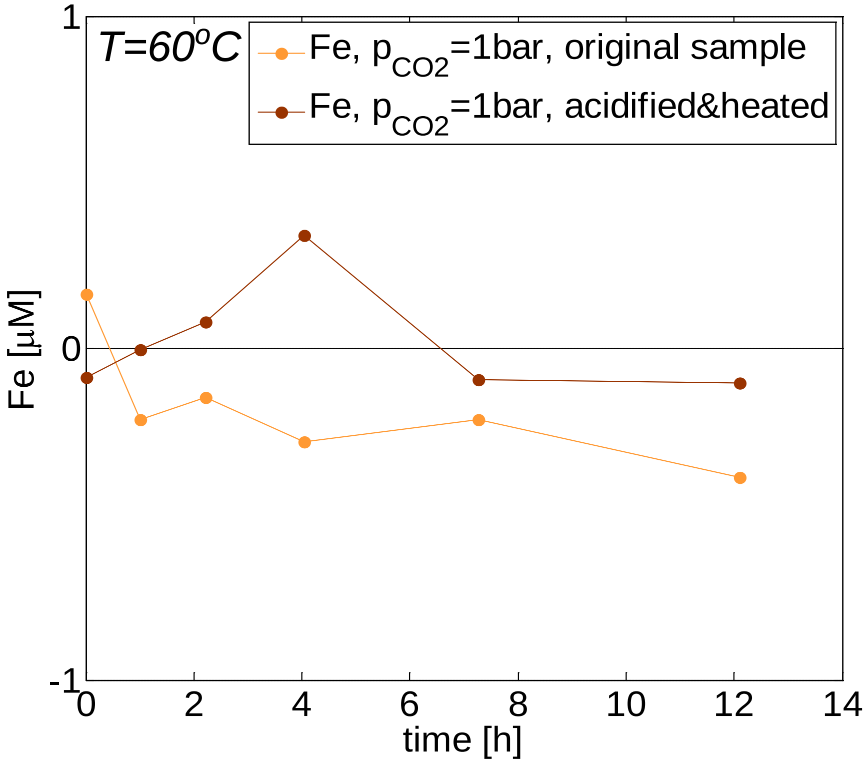
Dissolution model for activated serpentine

- Presence of micropores and altered crystal structure cause complex, incongruent dissolution behavior
- $Mg_{2.42}Fe_{0.58}Si_2O_5(OH)_4$ → **Iron** absent in reactor solution:



→ Preferential leaching of Mg^{2+}

Dissolution model for activated serpentine

- Presence of micropores and altered crystal structure cause complex, incongruent dissolution behavior

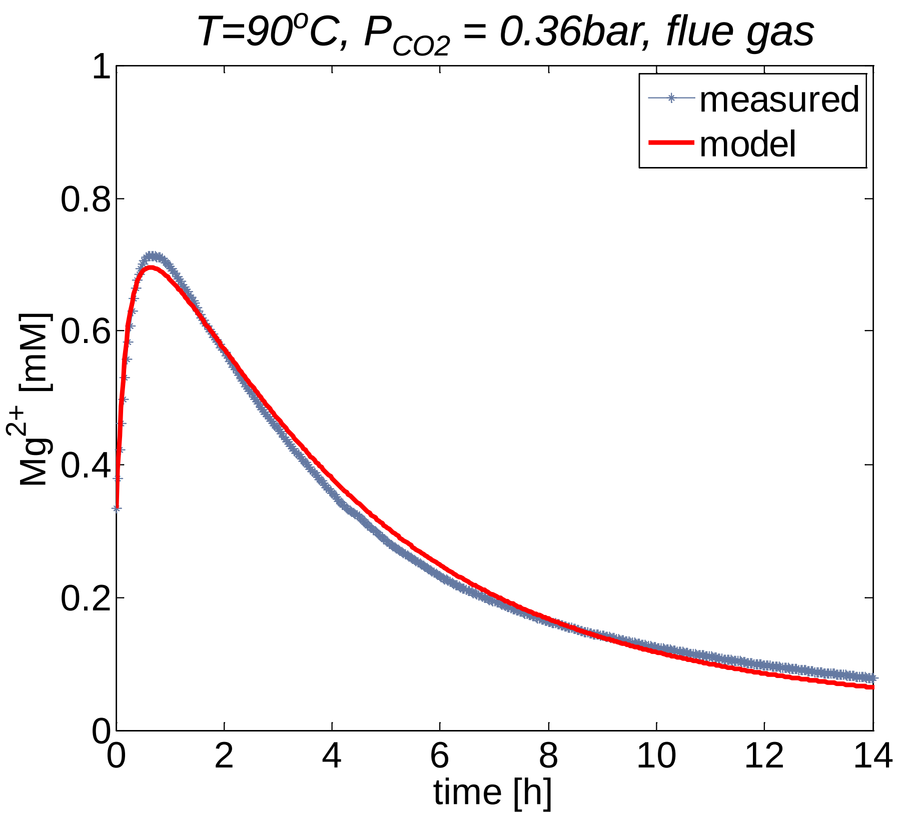
- Back to single particle model to explore the role of:

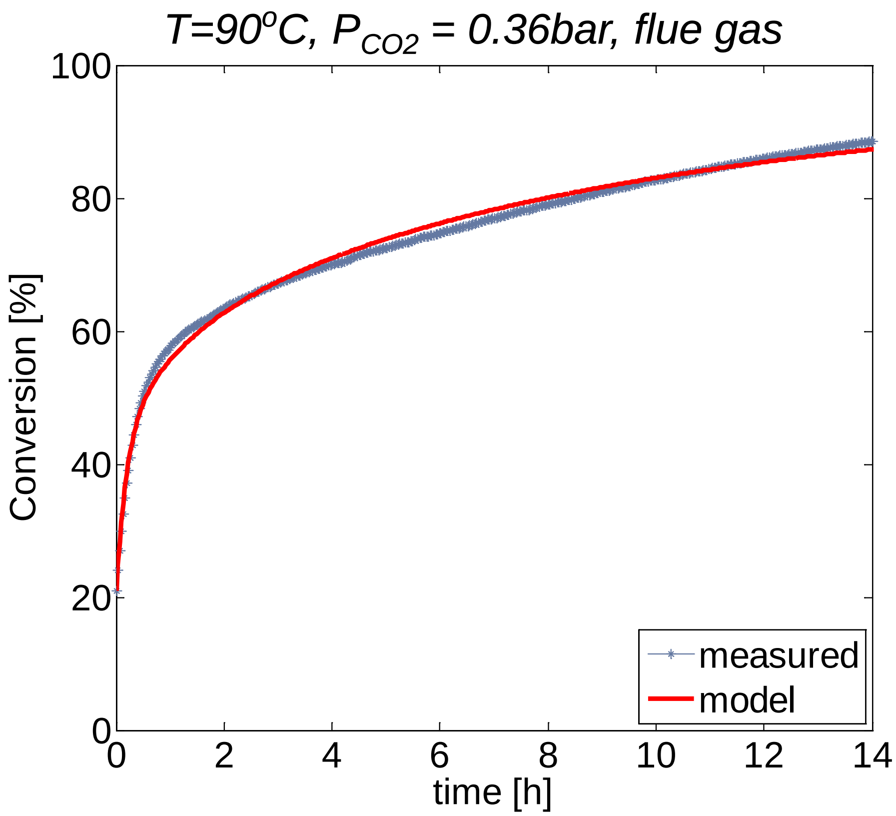
diffusion	ash layer	reactants (H^+)
	unreacted core	
counterdiffusion	pores	products (Mg^{2+}, silica)

- PSD discretized to perform preliminary simulations
- Single experiments can be fitted nicely, but fitting multiple exeriments yet an issue

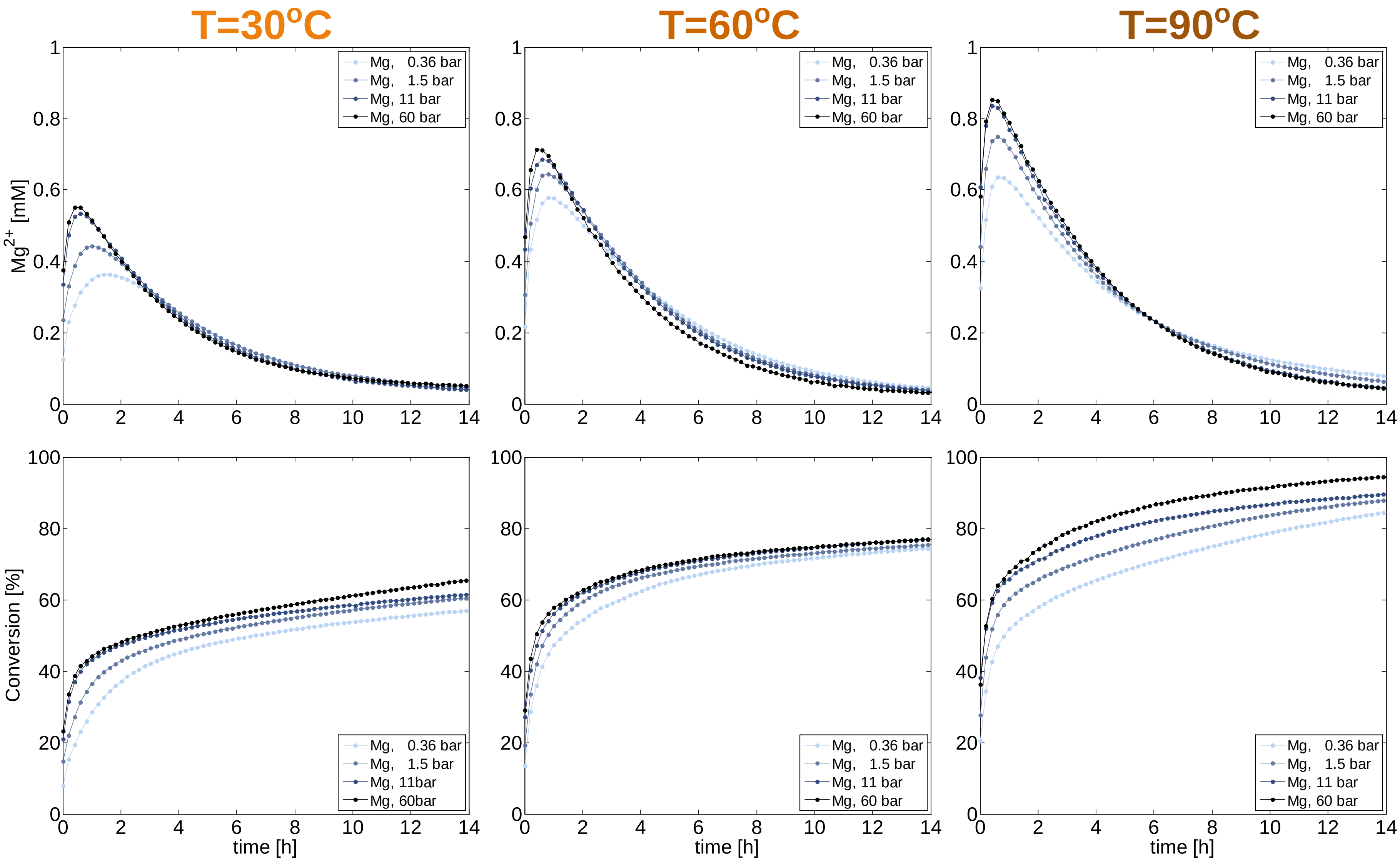
Dissolution model for activated serpentine

Measured and modelled Mg^{2+} profile and conversion:





Serpentine dissolution experiments



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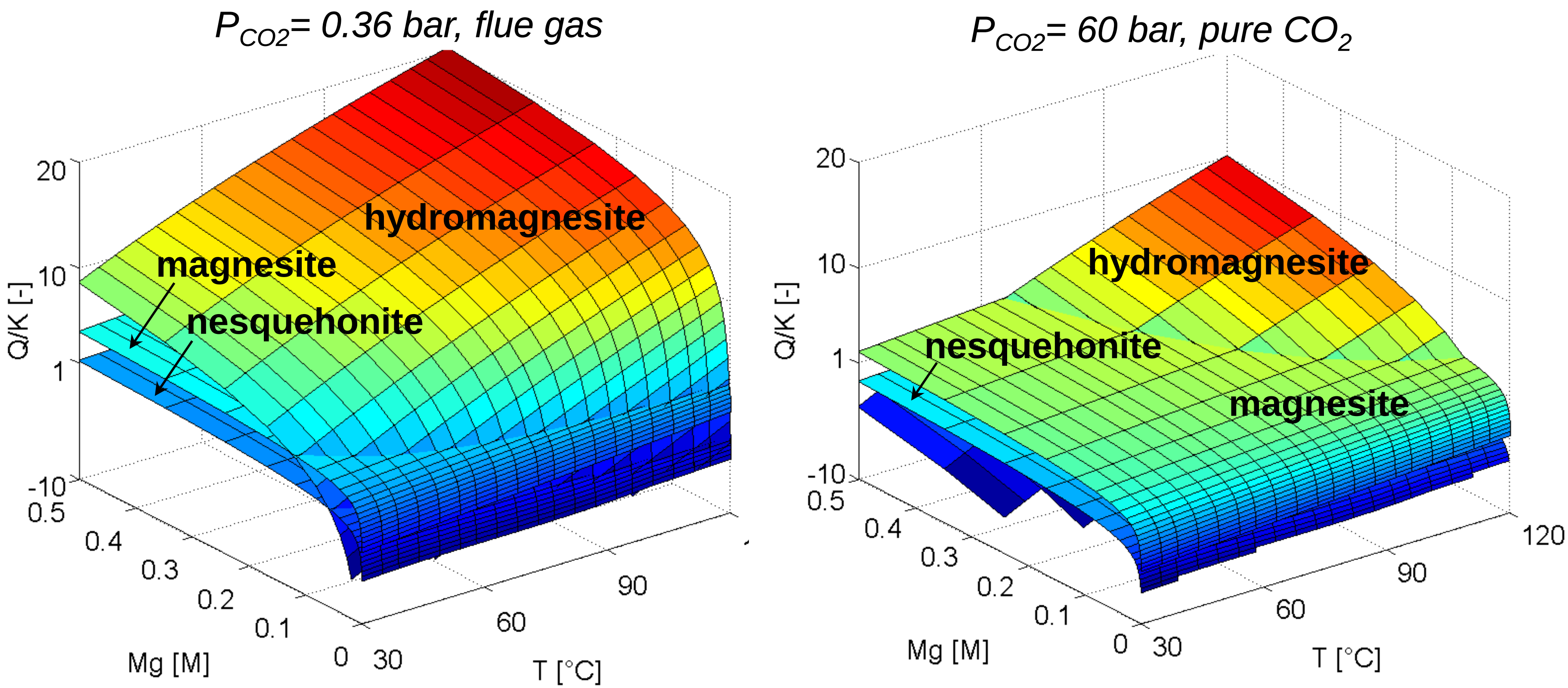
Storage part: EQ3/6 equilibrium simulations

Thermodynamic driving force (Q/K) as function of T and $[Mg^{2+}]$:



→ Higher T favors carbonate precipitation

→ High P_{CO_2} not beneficial, flue gas conditions preferable!

Concluding remarks

- CO_2 capture into aqueous solution promoted by presence of Mg^{2+} from the dissolution process
- Activated serpentine dissolution fast even at low P_{CO2}, thereby preferential leaching of Mg^{2+}
- Higher T promotes Mg leaching and reduces carbonate solubility
- Thermodynamic driving force for precipitation higher under flue gas conditions

Acknowledgements

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- Competence Center Energy and Mobility, CH
- Competence Center Environment and Sustainability, CH

Thanks for your attention

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