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Design of a hybrid leaching process for mineral carbonation of magnesium silicates: learnings and issues raised from combined experimental and geochemical modelling approaches

Carine Julcour¹, Florent Bourgeois¹, Laurent Cassayre¹, Julien Leclaire², Solène Touzé³, Martin Cyr⁴, France Bailly⁵

¹LGC, Toulouse, France ; ²ICBMS, Villeurbanne, France ; ³BRGM, Orléans, France ; ⁴LMDC, Toulouse, France ; ⁵CNRT, Nouméa, France



CO₂ CARMEX
 French National Research Agency
 ANR (ANR CO₂ 2009-2012)

*Worldwide potential of MC (GIS)
 Examination of MC mechanisms
 Proof of concept of selected MC route
 Environmental assessment (LCA)*



New-Caledonia as prime candidate for MC deployment



CARBOSCORIES I
 National Centre for Technology Research
 CNRT "Nickel and its environment"
 CNRT NICKEL (2015-2016)

*Potential of Ni slags for MC hybrid process
 Balance analysis for two metallurgy plants*



CO₂EMR
 Collaborative work

CARBOSCORIES II
 Caledonian Energy Agency
 (2018-2021)

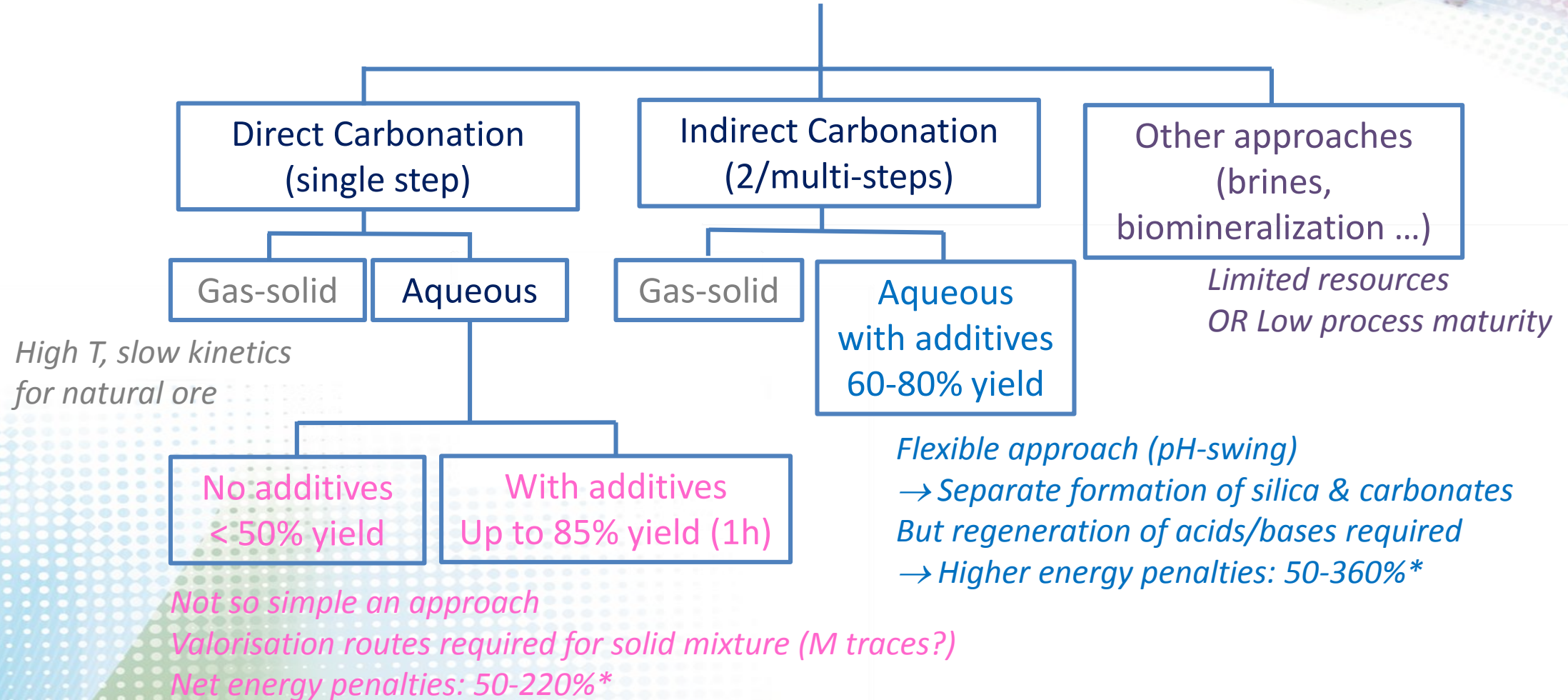


*Bench-scale continuous pilot
 Valorisation route for MC products*

CO₂ Enhanced Metal Recovery



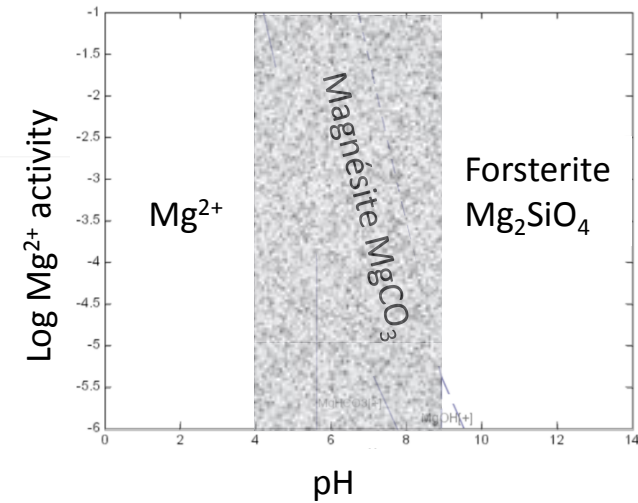
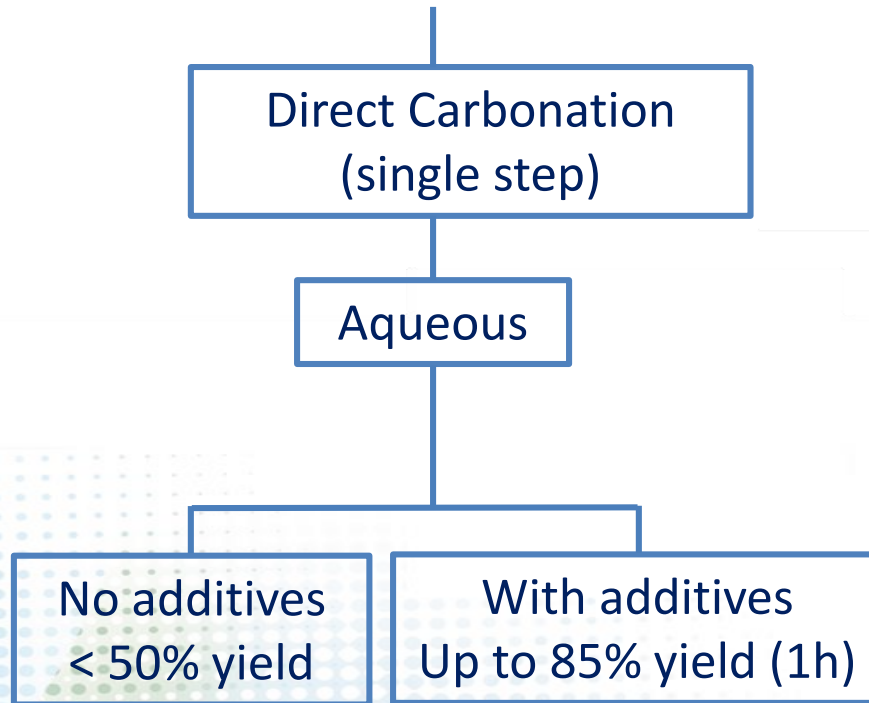
Ex-situ Mineral Carbonation pathways



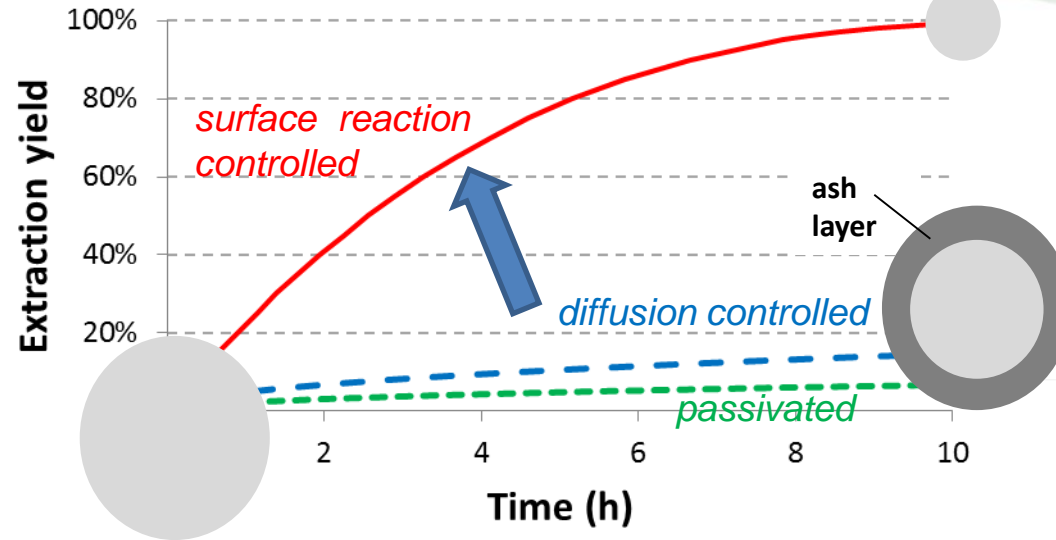
Adapted from *Sanna et al. (2014)*

*based on < 2010 literature routes for 154 MWe coal-fired power plant producing 1Mt-CO₂/yr

Studied MC pathways

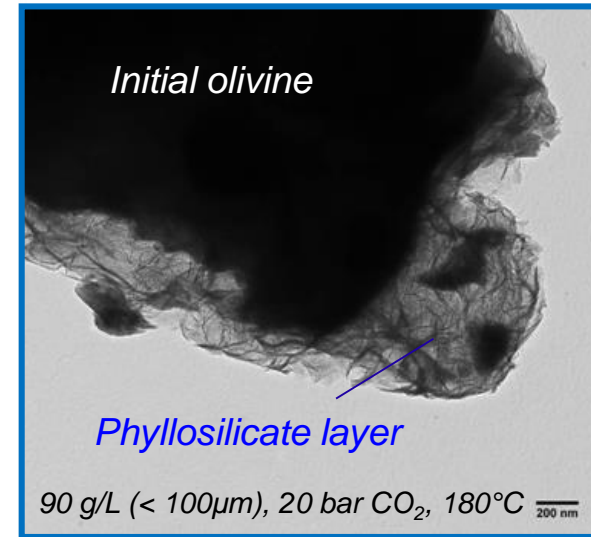
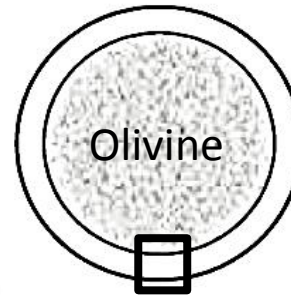
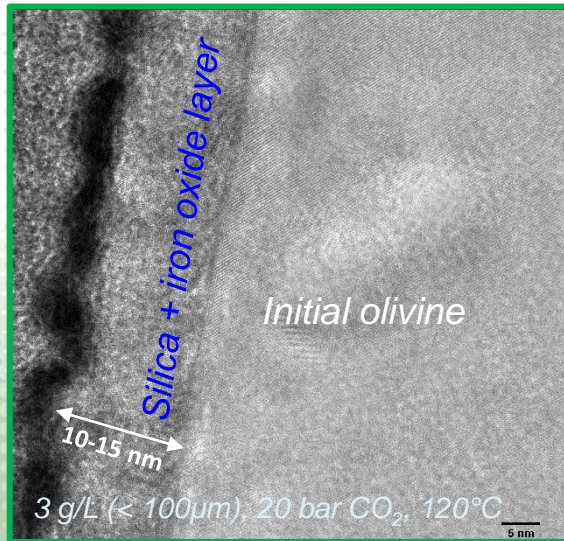


Surface leach layer & mechanisms



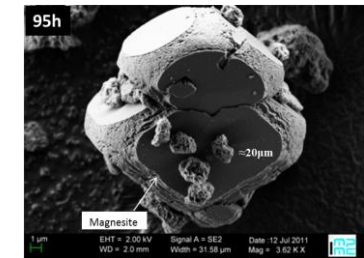
Passivating

→ No carbonate



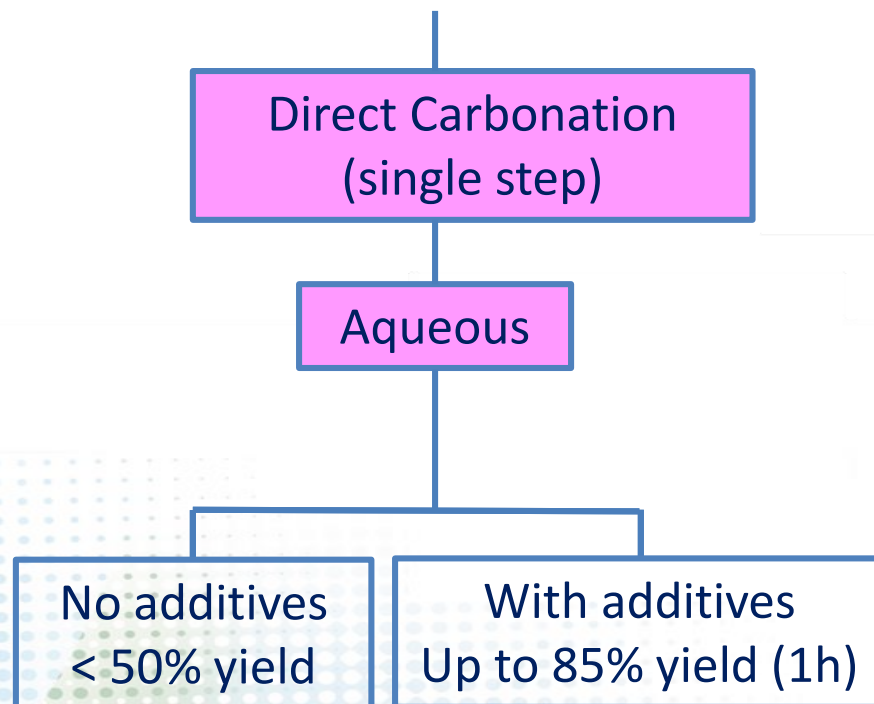
Diffusion controlling

Carbonation yield < 10% (90 g/L, 95 h)



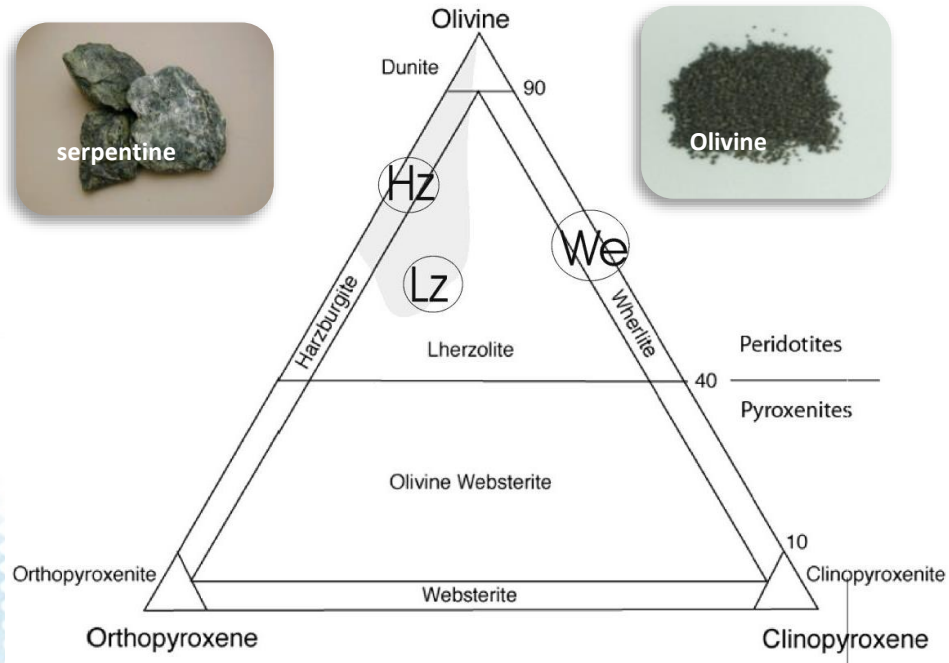
FIB cross-sections of olivine particle after leaching (TEM) (Bodenan et al., 2014)

Studied MC pathways



EXPERIMENTAL METHODOLOGY

Ores



Bodenan et al. (2014)

Serpentinisation degree up to 90%

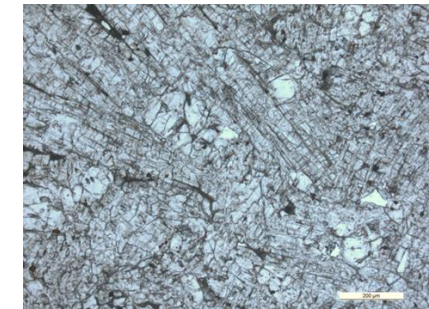
Name	Origin	Dominating phases
Harzburgite (Hz1)	New Caledonia	Serpentine (~ 90%) >> olivine > orthopyroxene
Harzburgite (Hz2)	New Caledonia	Serpentine (~ 90%) >> olivine > orthopyroxene
Wherlite (We)	New Caledonia	Serpentine (~ 50%) > olivine > clinopyroxene
Lherzolite (Lz)	France (Pyrenees)	Serpentine (~ 50%) > olivine > clino/ortho-pyroxene
Olivine	Austria (Magnolithe)	Synthetic olivine (from high T dunite processing)

30.8 < MgO < 47.4%, 39.3 < SiO₂ < 46.3%, 7.3 < Fe₂O_{3tot} < 9.8%,
0.2 < CaO < 5.0%, 0.2 < Al₂O₃ < 4.0%

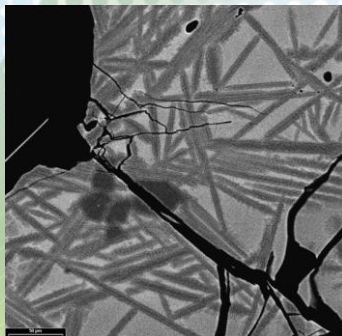
Slags



From Ni pyrometallurgy plant (Koniambo)
KNS slowly cooled under ambient conditions, SLN quenched by seawater



Name	Origin	Dominating phases
KNS	New Caledonia	Pyroxene: proto-enstatite, clinoenstatite, forsterite
SLN	New Caledonia	Vitreous fraction >> olivine



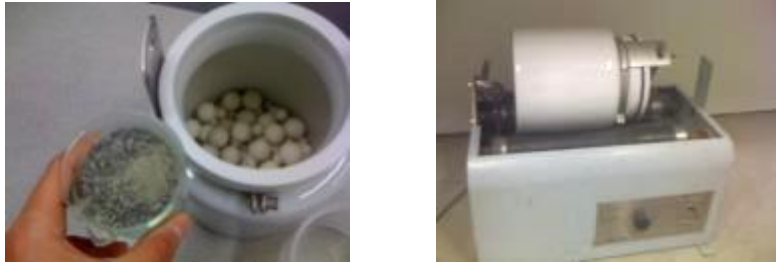
MgO ~ 30%, SiO₂ ~ 52%, Fe₂O₃tot ~ 13%,
CaO < 0.5%, Al₂O₃ ~ 2%

Solid preparation

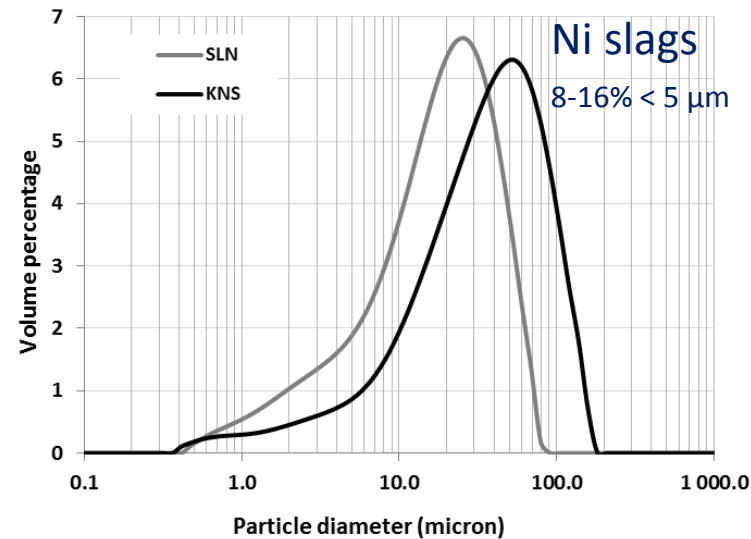
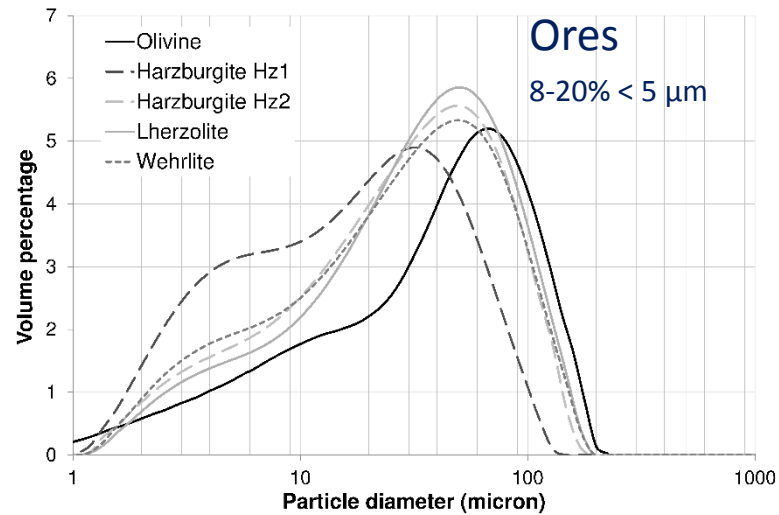
➤ Mechanical sampling



➤ Grinding (4h in ball mill) & sieving < 100 μm

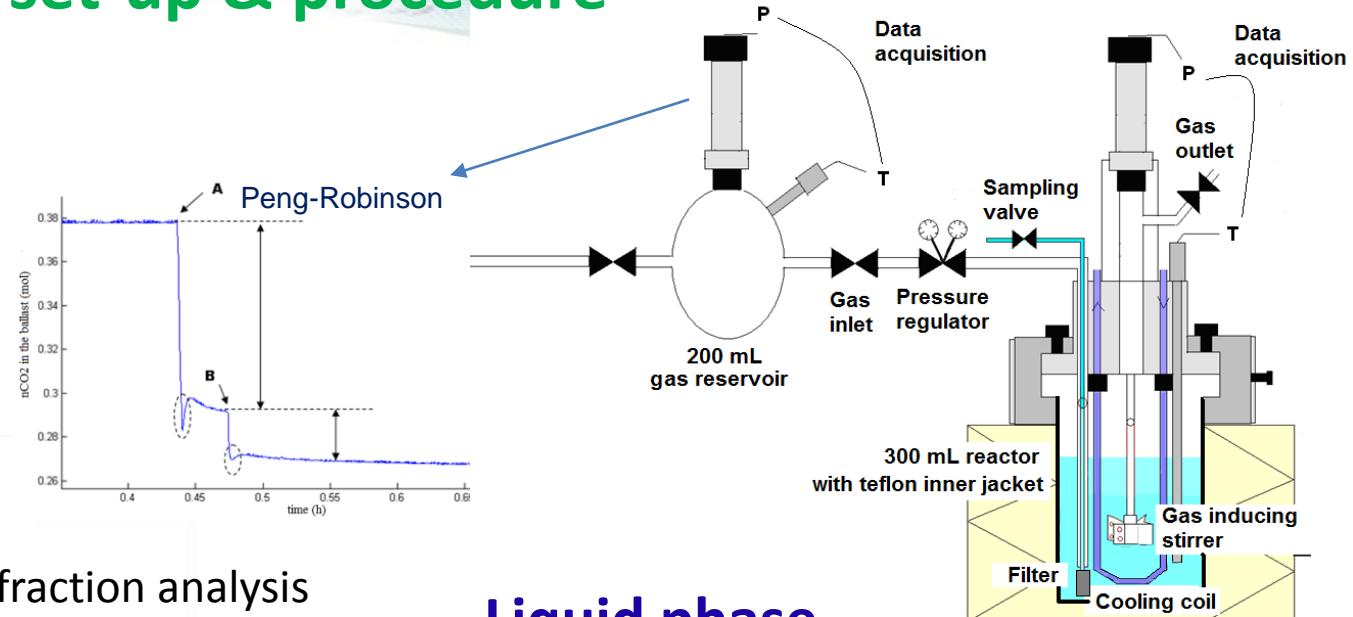


➤ Initial particle size distribution

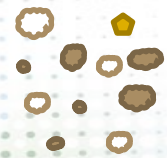


Carbonation set-up & procedure

- 300 mL autoclave reactor
- Controlled atmosphere (P_{CO_2}) and T
- Gas auto-dispersing stirrer (800 rpm)
- Continuous recording of CO_2 consumption (24 h)

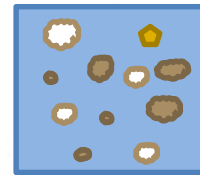


Solid phase



drying (70°C)

Laser diffraction analysis
Filtration (0.2 μ m)



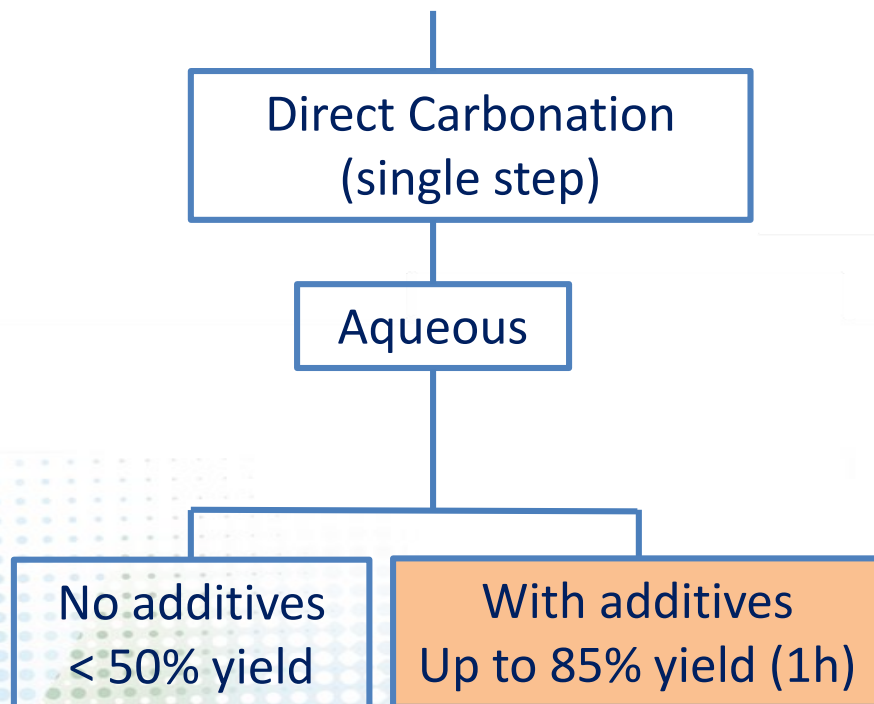
Liquid phase



- Identification of solids formed: SEM(TEM)/EDX and elemental mapping (Mg, Si, O), X-Ray Diffraction, Raman and IR (DRIFT) Spectroscopy, ICP/AES (after acid dissolution)
- Quantification of carbonated products: elemental analysis (C content), ThermoGravimetry Analysis coupled with IR

- Quantification of dissolved elements: ICP/AES (Mg, Si, Fe), inorganic carbon

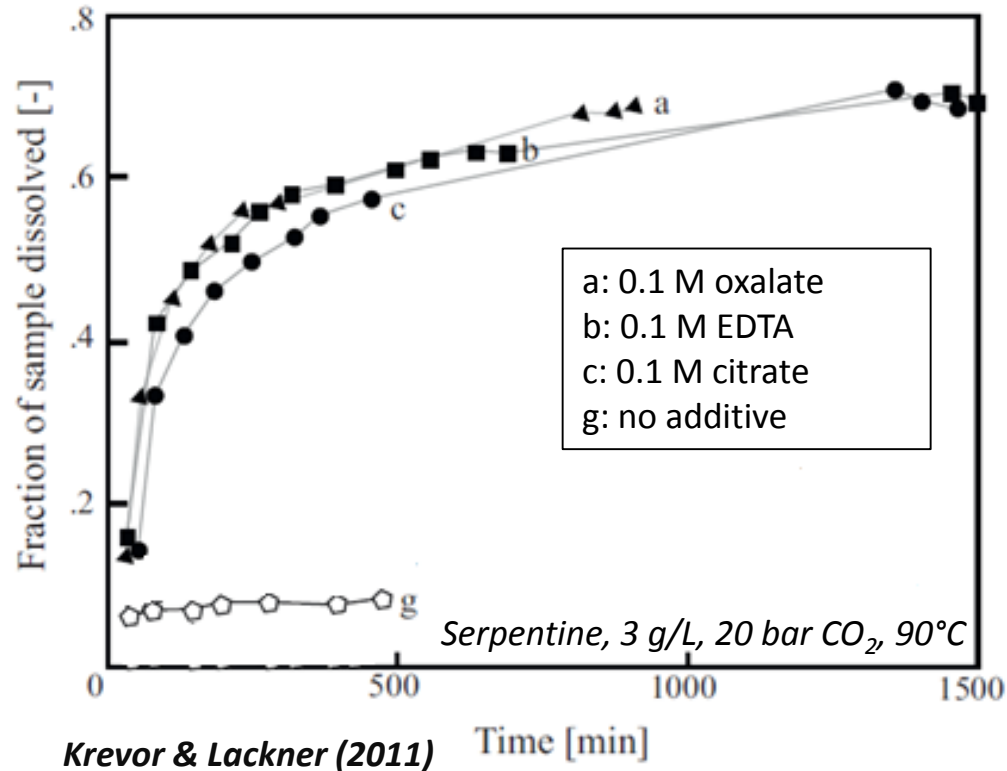
Studied MC pathway



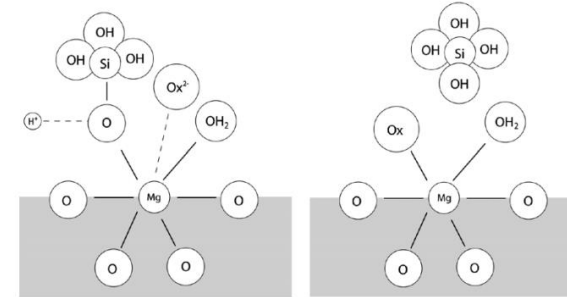
CHELATING AGENT APPROACH

State of the art

➤ Effect of organic polyacids on dissolution rate



➤ Mechanism



Olsen & Rimstidt (2008)

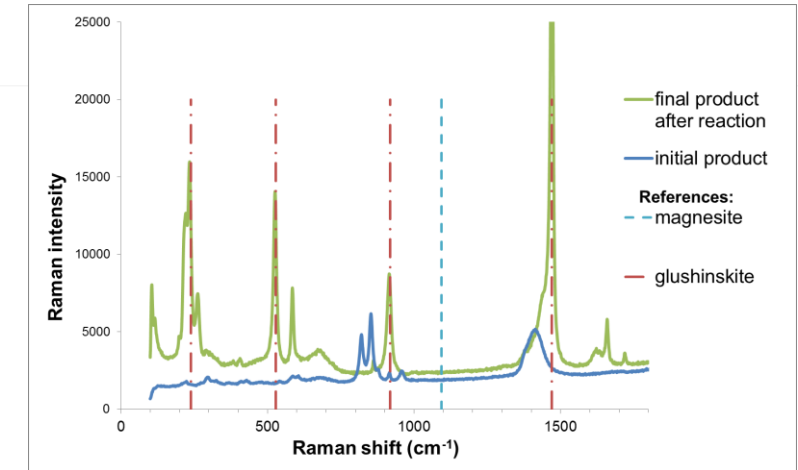
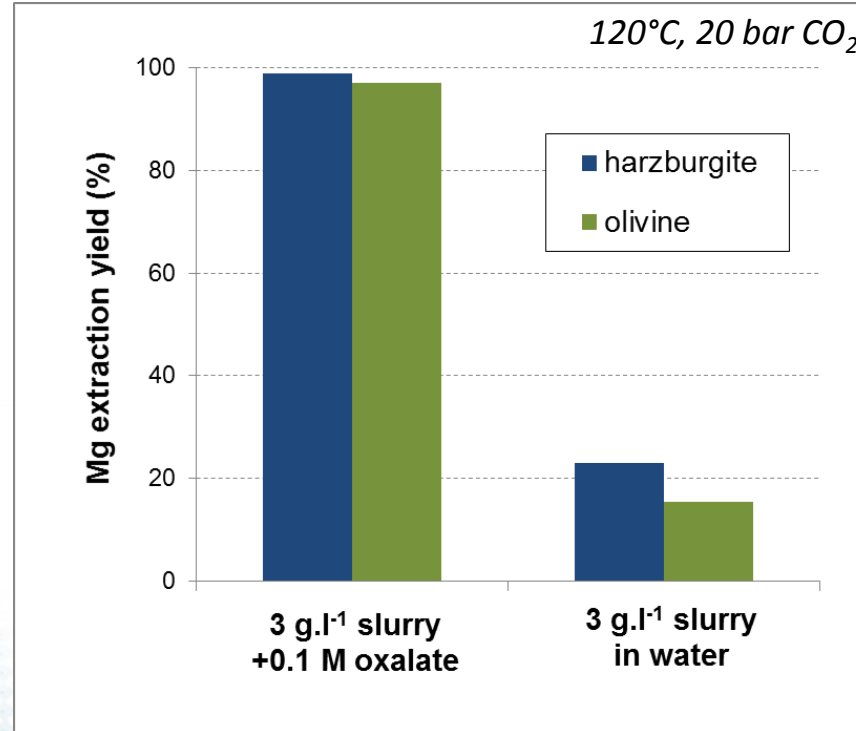
➤ Oxalate-enhanced dissolution rate

$$r = \left(\frac{1 + \beta K_x a_{ox}}{1 + K_x a_{ox}} \right) r_{H^+}$$

≈ 7 at 0.1 M oxalate (olivine, pH 5, 120°C)

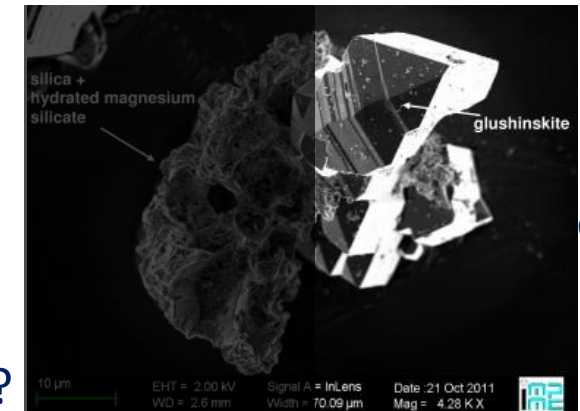
Prigiobbe & Mazzotti (2011)

Oxalate-enhanced dissolution of olivine: leaching yield & Mg speciation

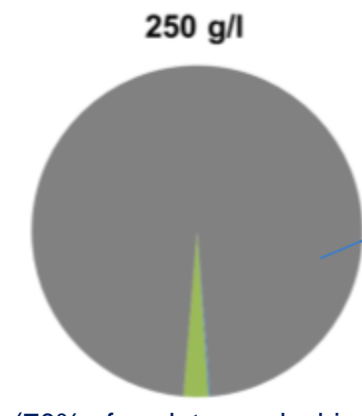
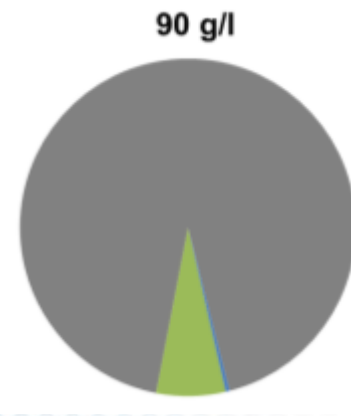
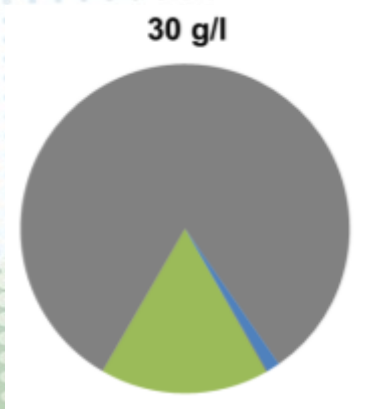
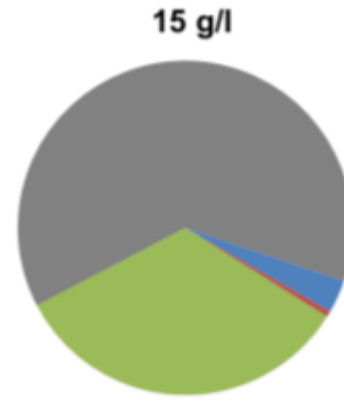
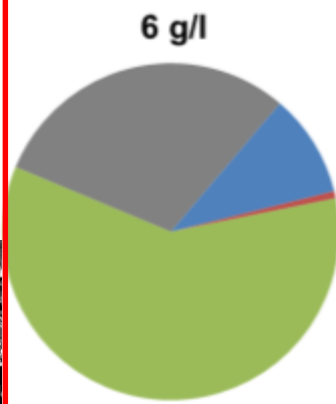
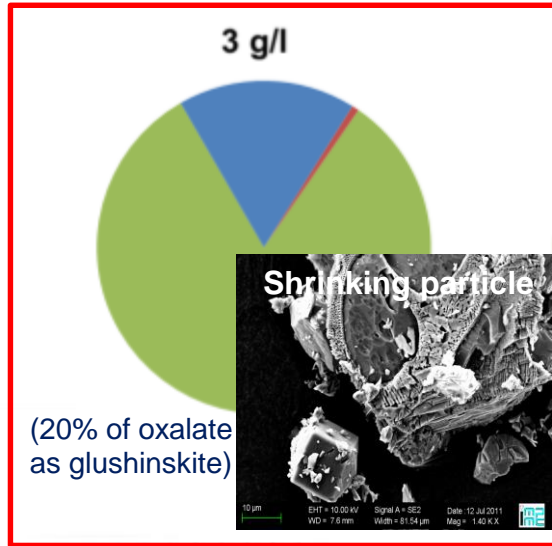


➤ Significantly improved extraction yield with oxalate at 3 g/L, but formation of solid by-product: **glushinskite** (MgC₂O₄.2H₂O)

➤ Any compromise between glushinskite precipitation & Mg carbonation?



Oxalate-enhanced dissolution of olivine: effect of slurry concentration



(70% of oxalate as glushinskite)

Mg speciation after 24h

120°C, 20 bar CO₂,
olivine < 100 μm,
speciation after cooling

- Carbonates
- Glushinskite
- Olivine
- Solution

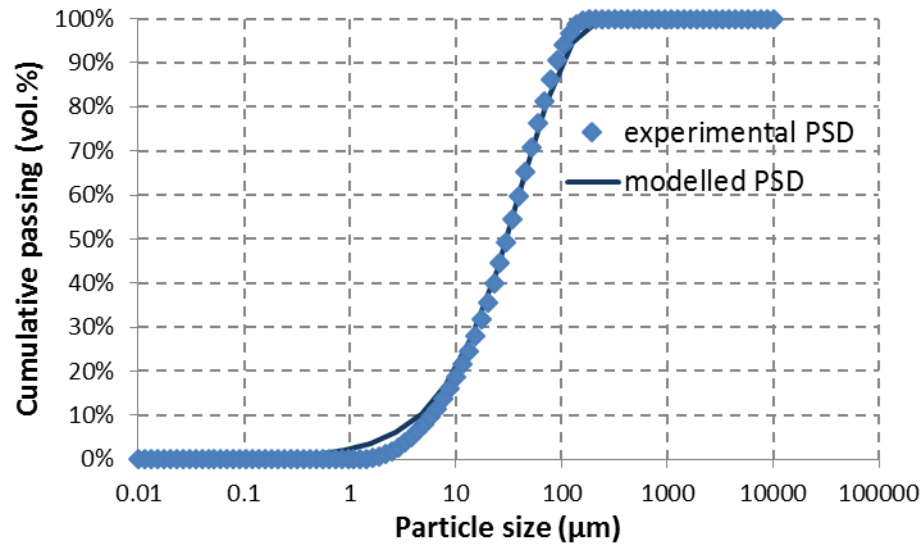
- Carbonation yield < 1% → not a viable option in these conditions
- Could geochemical modeling predict such competing effects?



Oxalate-enhanced dissolution of olivine: kinetic modeling

Rate-limiting step: ore dissolution (instant. gas absorption & solid precipitation)

~20 size classes (SSA_{0i} , m_{0i}) generated from Rosin Rammler PSD model



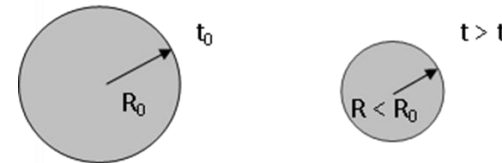
(α & d_{90} parameters fitted to match experimental PSD)

Shrinking particle model

$$\frac{dn_i}{dt} = -r \cdot SSA_{0i} \cdot m_{0i} \left(\frac{n_i(t)}{n_{i0}} \right)^{2/3}$$

$$r = \left(\frac{1 + \beta K_x a_{ox}}{1 + K_x a_{ox}} \right) r_{H^+}$$

$$r_{H^+} = k_0 \cdot \exp(-E_a/RT) \cdot a_{(H^+)}^n (1 - 10^{SI})$$

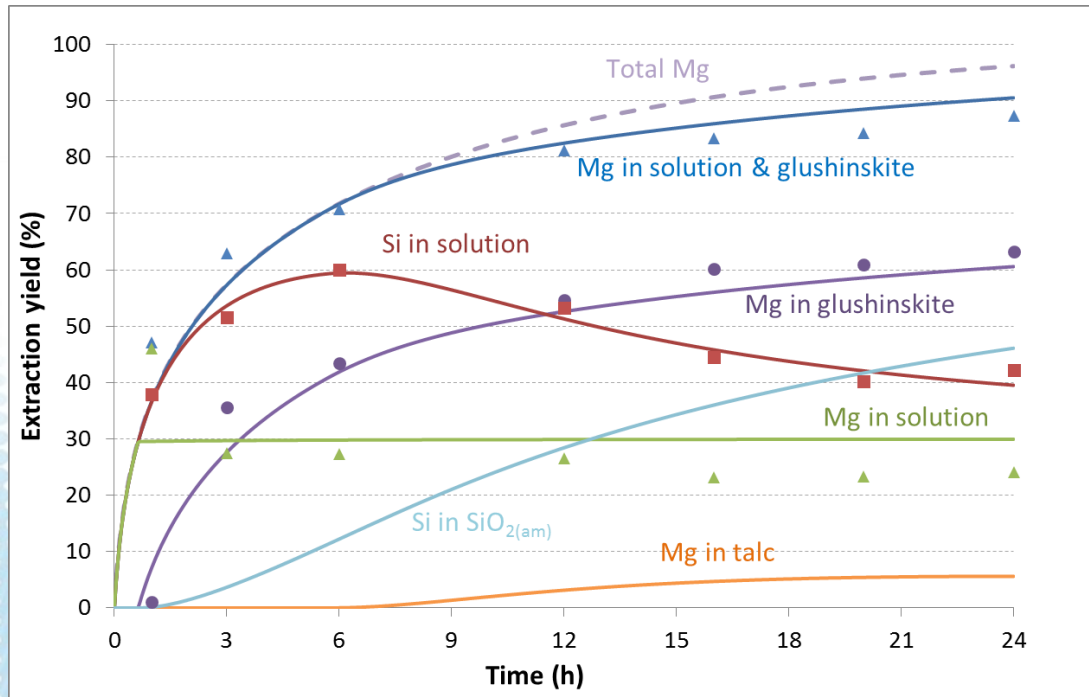


surface reaction rate from Prigiobbe & Mazzotti (2011)



Oxalate-enhanced dissolution of olivine: geochemical modeling (with CHES)

- Issues:**
- Mg-oxalate species missing in used thermodynamic database (CTDP)
 - Glushinskite equilibrium data only available at 25°C
- dedicated precipitation experiments at 120°C & **database updating**



Bonfils et al. (2012)

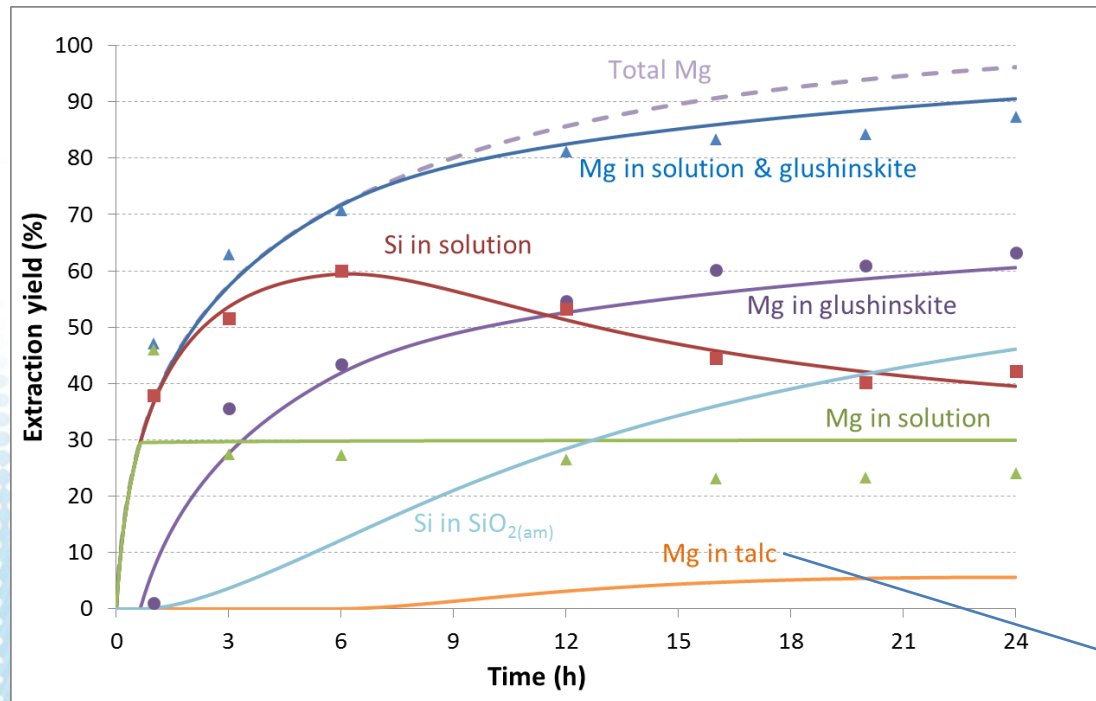
- Good agreement with experimental data at 3 g/L
→ chemical controlled reaction

120°C, 20 bar CO₂,
3 g/L olivine < 100 μm

Simulation with CHES
code (*van der Lee, 2007*)
after estimation of
precipitation rate
constants for silica & talc

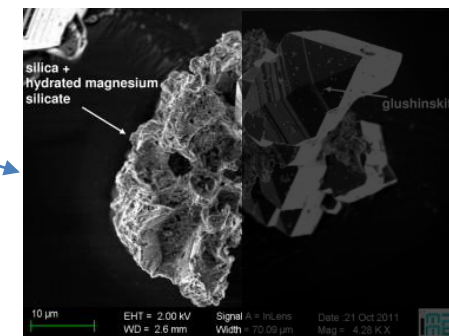
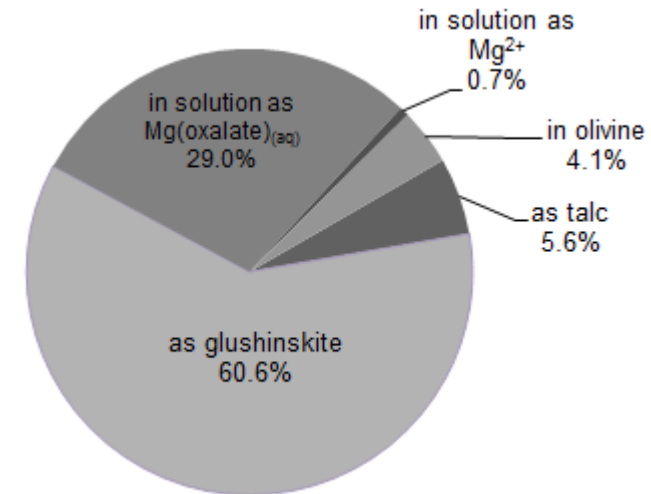
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Bonfils et al. (2012)

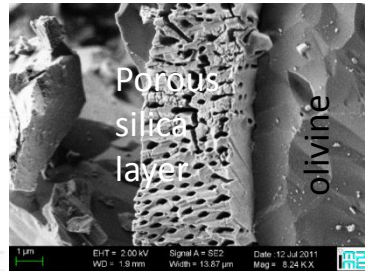
- Good agreement with experimental data at 3 g/L
- chemical controlled reaction



Learnings & issues

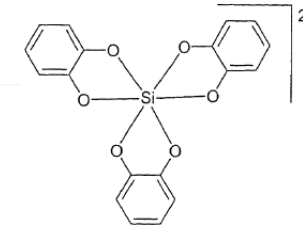
- Organic polyacid salts (oxalate, citrate, EDTA): too strong Mg binders for MC at moderate P_{CO_2}
- Alternative option: silica(te) layer modulation / impeding by ligands

Oxalate



Catechol

Carbonation yield increased from 9.6% after 95 h (water) to 14.5% after 75 h (0.5 M catechol)



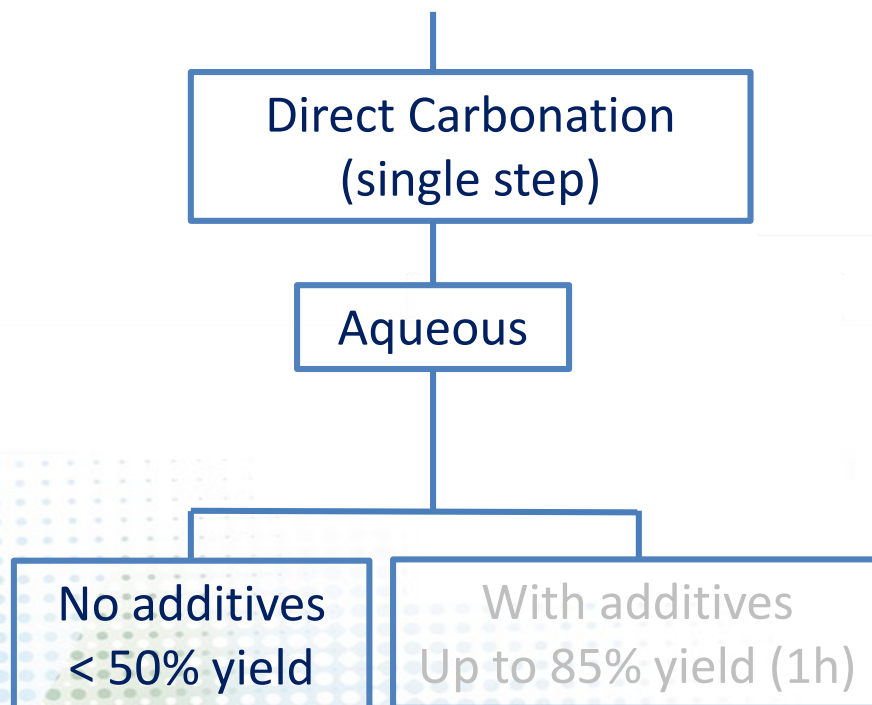
Si-catechol complex

(*Barnum, 1970;*
Russo-Mascioli, 2001)

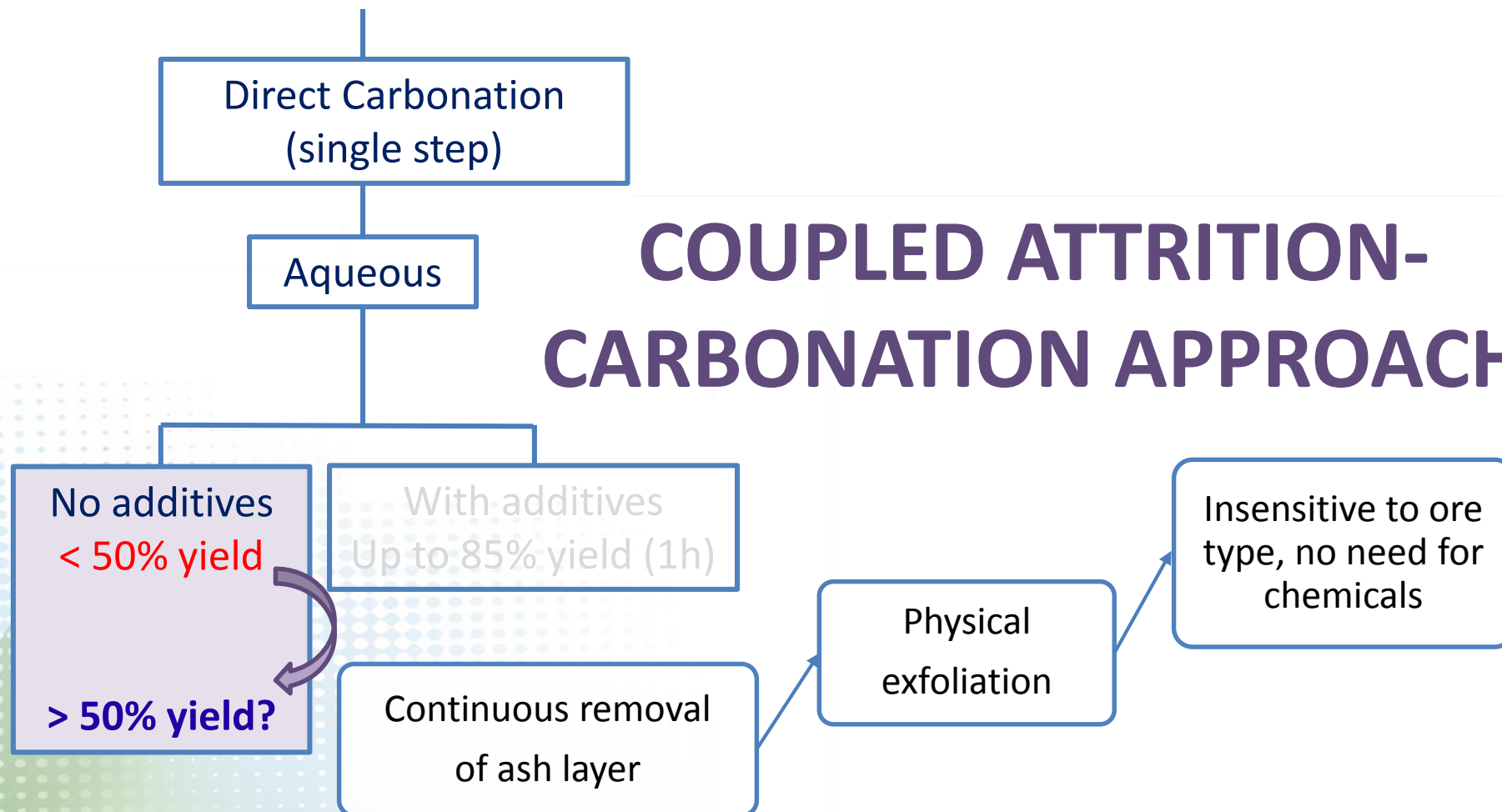
but might be ore-sensitive (complexation with Fe, Al ...)

- Exhaustive analysis of both liquid & solid products = MANDATORY
- Geochemical modeling as a valuable tool to predict effect of all inputs, but
 - * careful selection & analysis of thermodynamic database required
 - * going from & to experimental data needed

Studied MC pathways

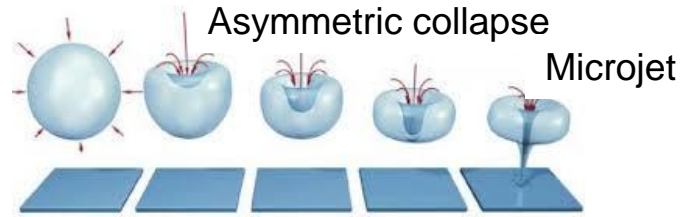


Studied MC pathways



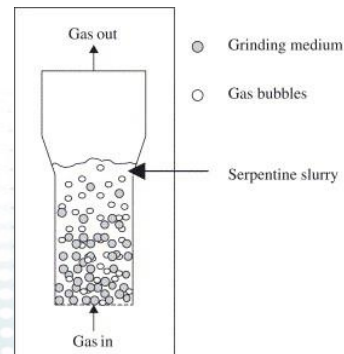
State of the art

- **High power ultrasound**

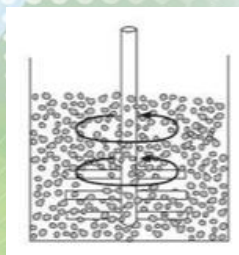


<http://eswt.net/cavitation> **Solid surface**

- **Fluidized bed with grinding medium**



- **Stirred tank with abrasive particles**



- Enhanced carbonation yield (with quartz particles up to 60 wt.%)

Santos et al., 2011-2013; McKelvy et al., 2004; Park & Fan, 2004

Can be operated at moderate P (< 10 bar),
but dampened under high T (> 50 °C)
→ mainly in a sequential process

- Mixed results

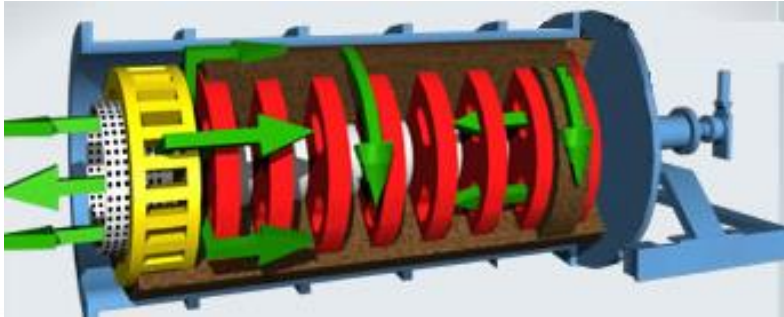
Park & Fan, 2004

Might be difficult to control (density and/or size differences between reactive & inert particles),
limited amount of grinding medium (20 wt.%)

- Some improvement of ore dissolution

Chizmeshya et al., 2007

Proposed technical solution: stirred ball mill



IsaMill™ (Netzsch)

Advantages:

- ✓ proven technology at large scale
- ✓ slurry conc.: up to 40%
- ✓ feed PSD: from μm to mm size range
- ✓ operability under high T & high P
- ✓ scalability from 4 L to 50 m³

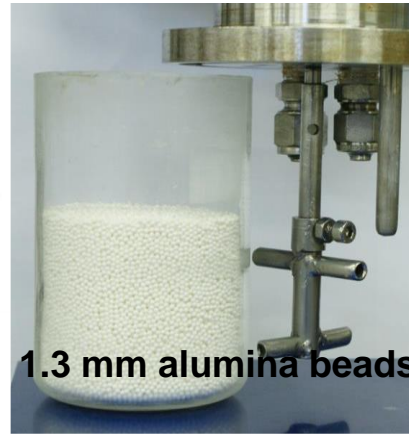
Issues:

- (long-term) exfoliation efficiency?
significant carbonation yield?
within a reasonable solid residence time?
- passivation layer attrition vs. breakage of ore particles?

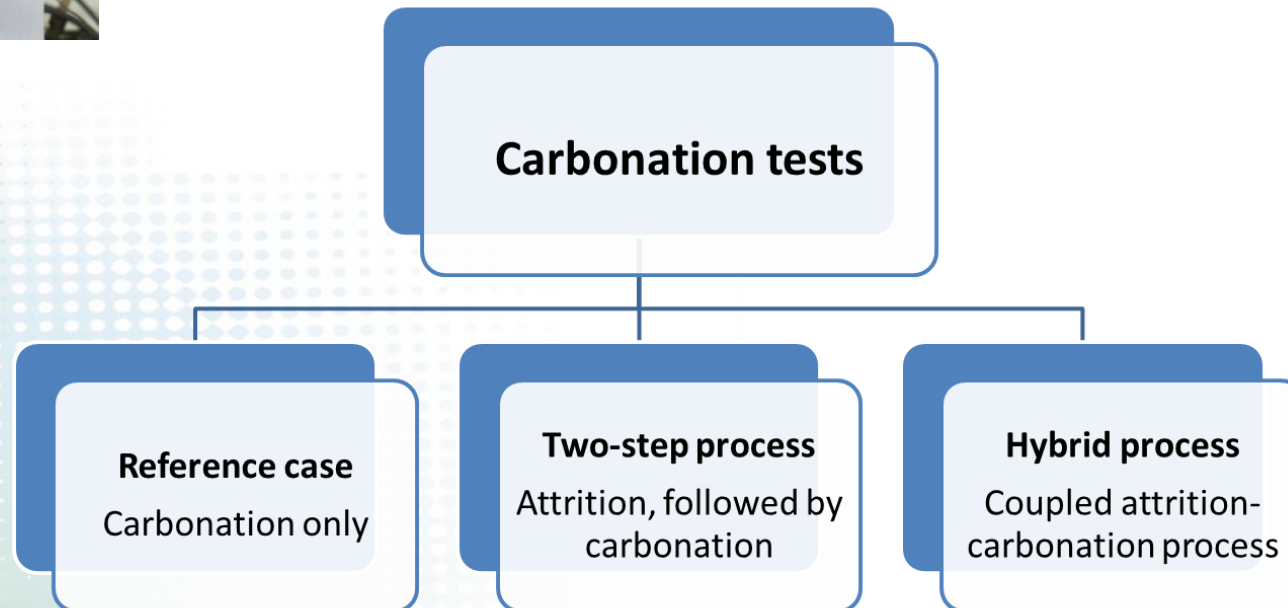
↓
energy efficiency: matching attrition process with passivation process?

Proof of concept

Grinding media: 90 mL of 1-2 mm beads
+ 80 mL of slurry (90-250 g/L) – $\omega = 800$ rpm



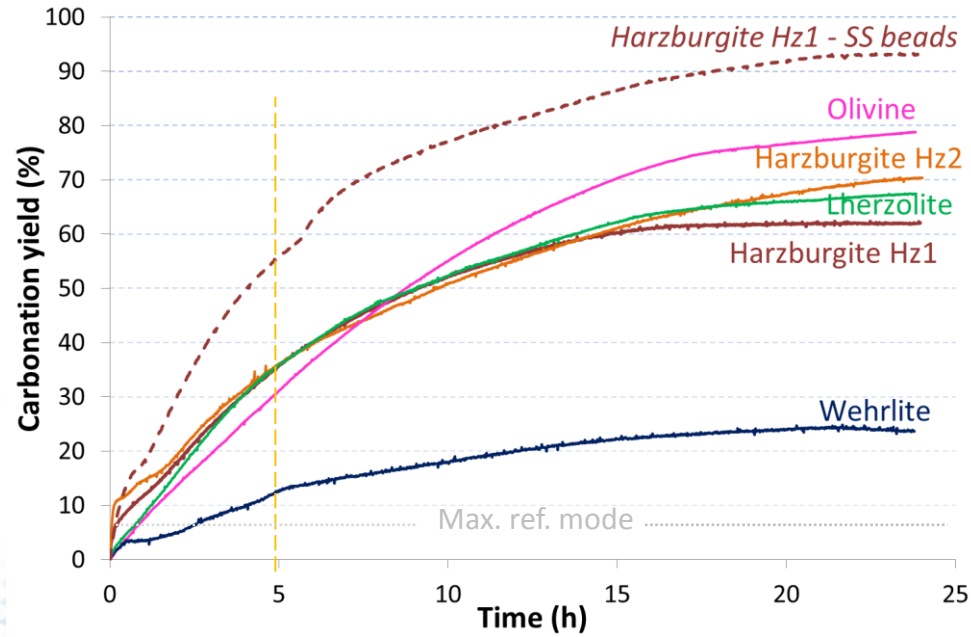
1.25-1.6 mm sand particles (99% SiO₂)





Proof of concept

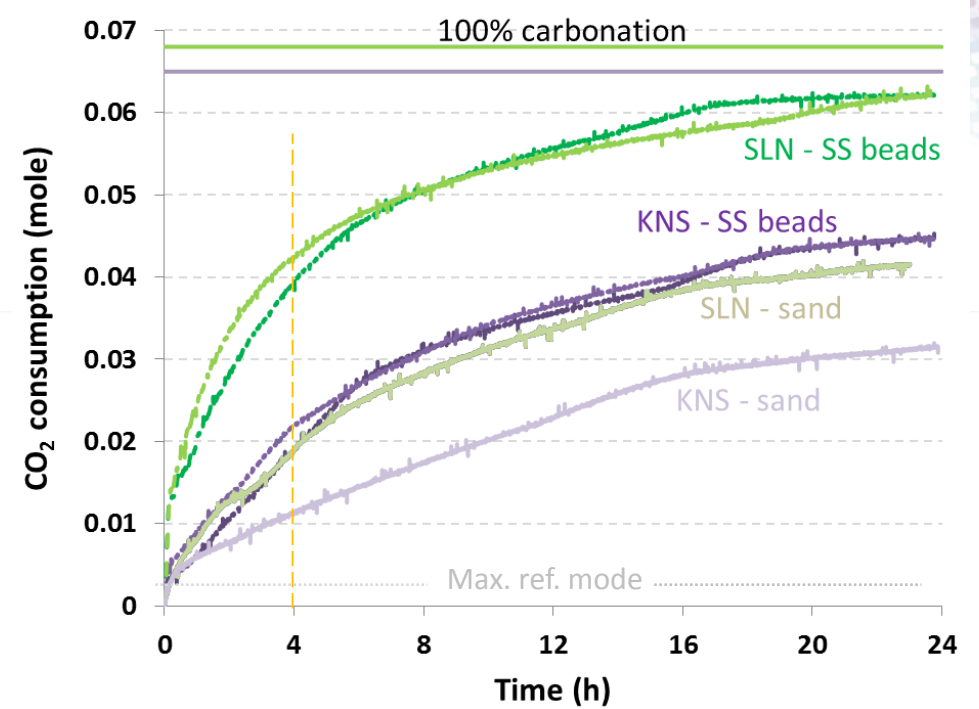
Ores



Extent of carbonation for different ore types
 (180°C, 20 bar CO₂, ore conc.: 90 g/L,
 1-2 mm Al₂O₃ — or SS grinding media ---)

- Significant extent of carbonation
 (vs. < 8% in 24 h without attrition)
- Almost insensitive to ore type
- Noticeable influence of grinding medium

Slags

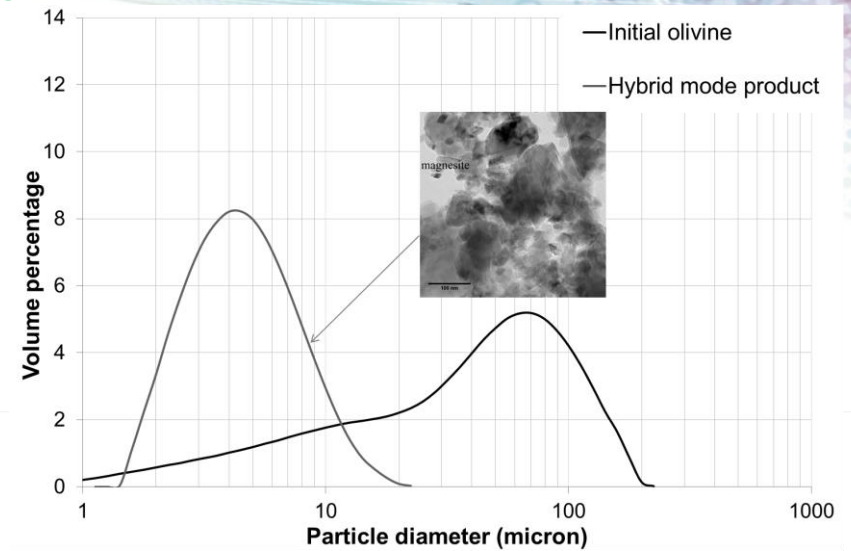


Extent of carbonation for different slag types
 (180°C, 20 bar CO₂, ore conc.: 90 g/L,
 1-2 mm sand — or SS grinding media ---)



Proof of concept

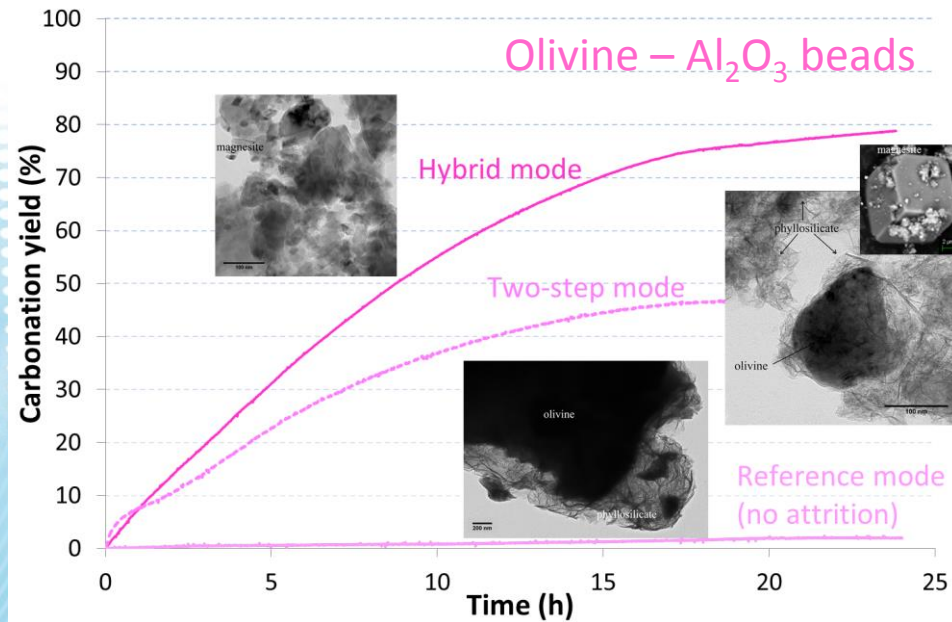
Size effect only?



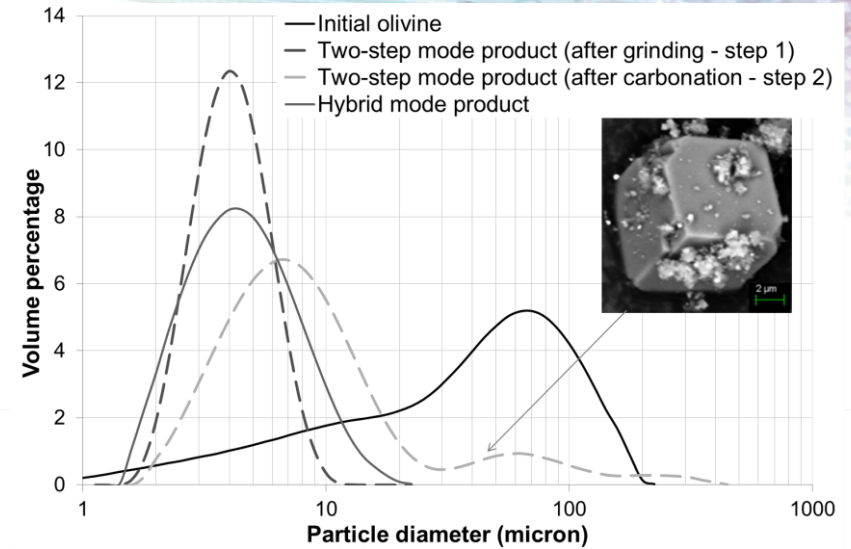
Proof of concept

Size effect only?

- Proof of synergy between attrition and leaching



180°C, 20 bar CO₂, ore conc.: 90 g/L

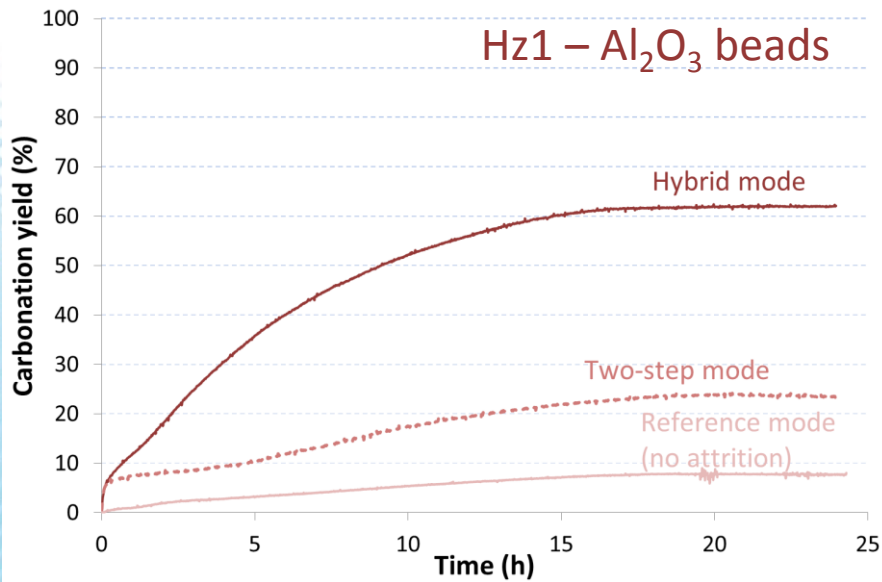
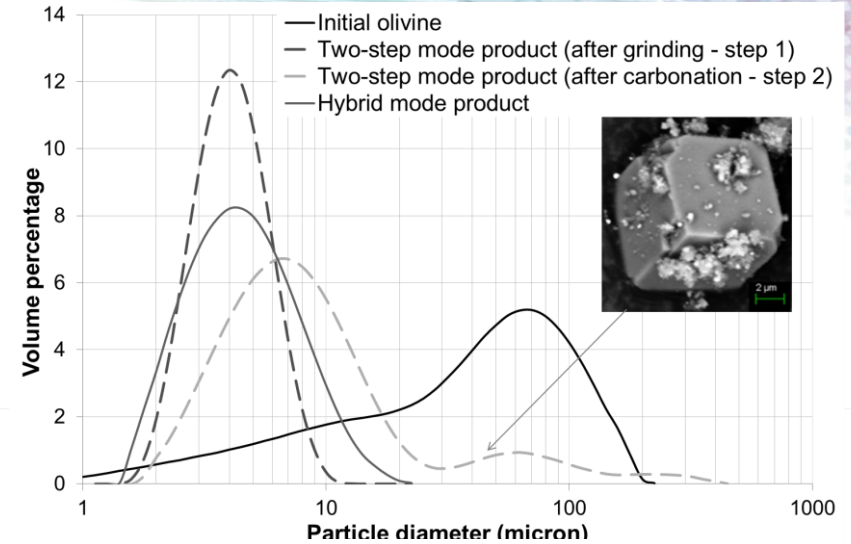




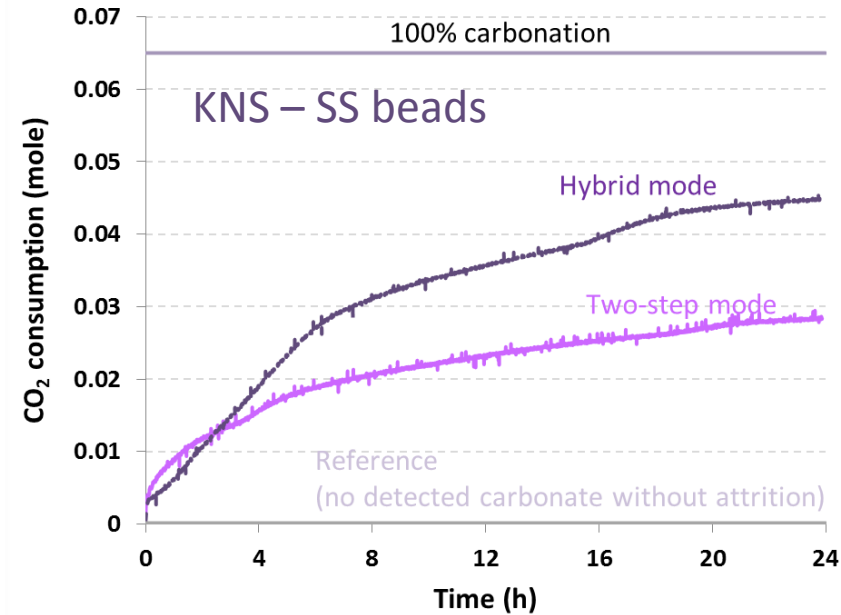
Proof of concept

Size effect only?

➤ Proof of synergy between attrition and leaching



180°C, 20 bar CO₂, ore conc.: 90 g/L



Life Cycle Assessment (LCA)

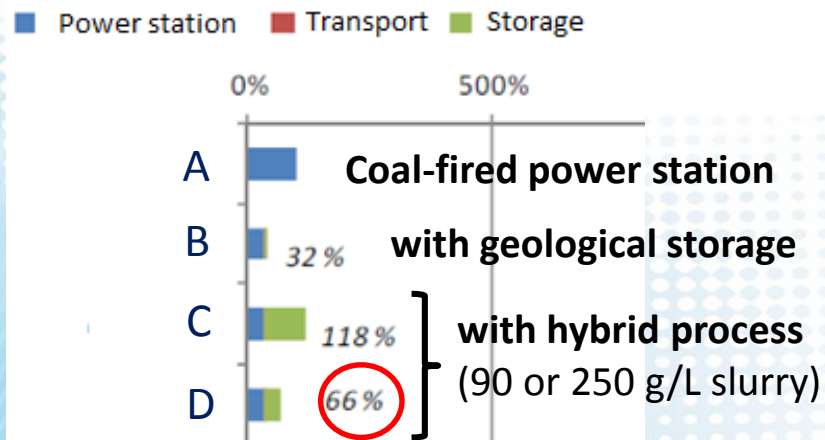
Functional unit: 1 MWhe with a coal-fired power station

Main hypotheses:

- yield of ~ 80% in 24 h at 20 bar CO₂ & 180°C
- CO₂ pipeline transport over a 300 km distance
- no recycling of process solution; no valorization of products

Impacts accounted for:

- CO₂ capture & compression
- crushing & milling of ore from 1 cm down to 100 μm
- mechanical energy expended for attrition
- reactants pre-heating & cooling (after heat integration)

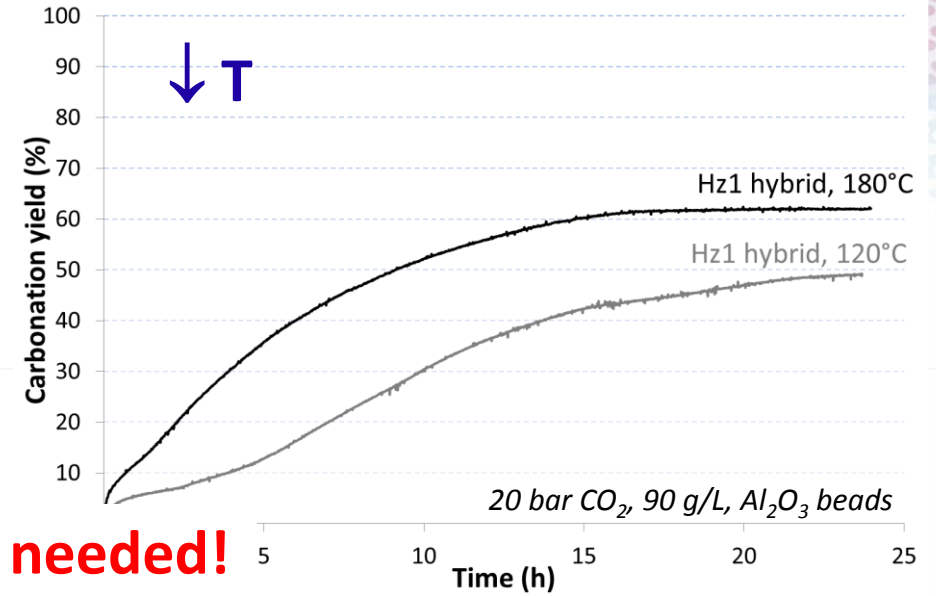
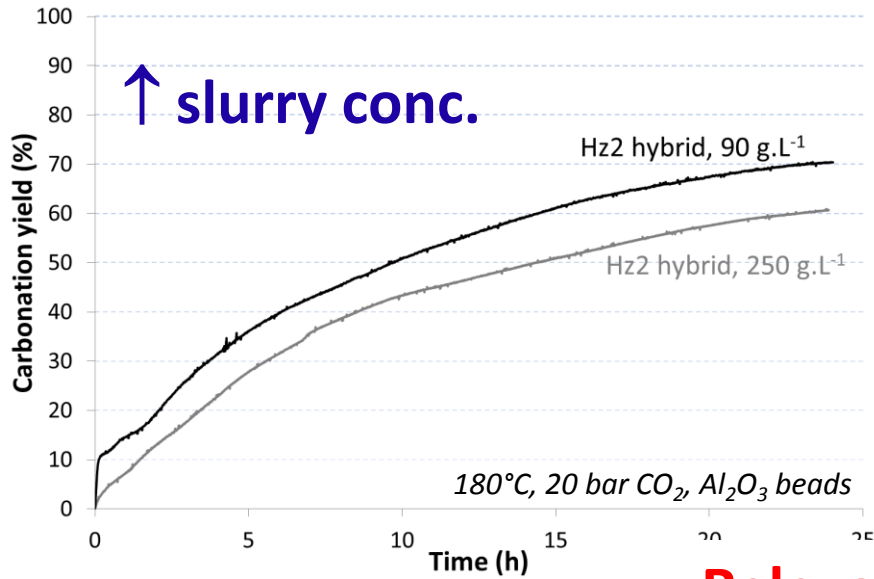


Net global warming potential (kg CO₂-eq)

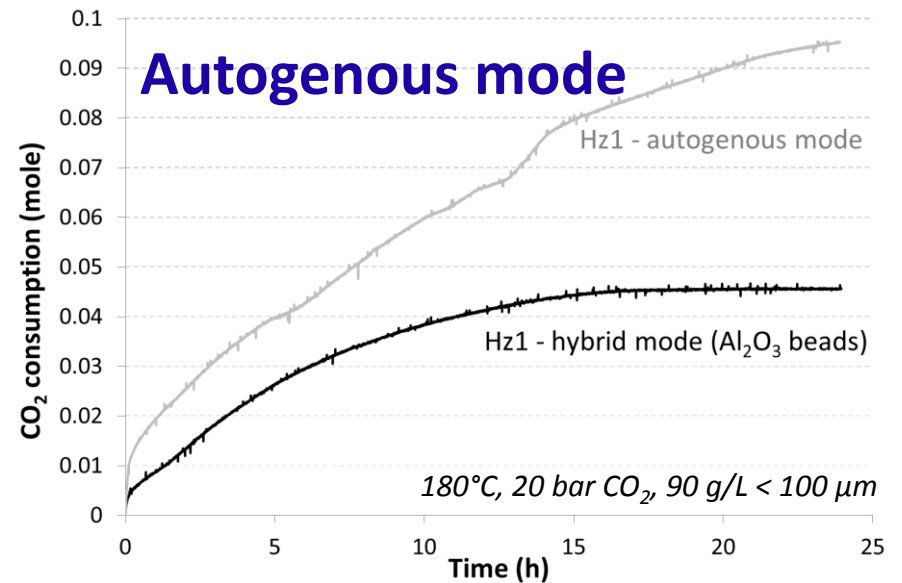
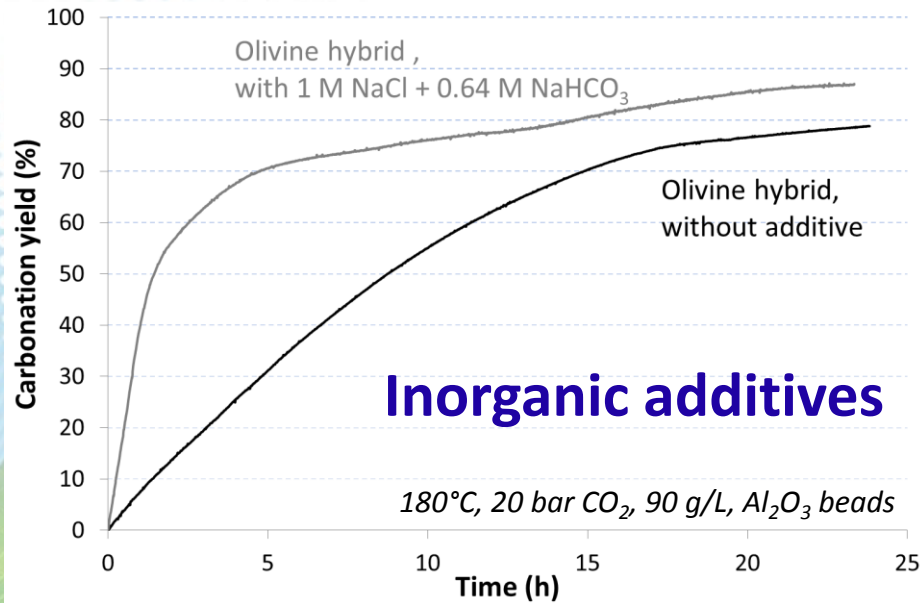
- Promising results regarding CO₂ avoided, without any process optimization
- Beneficiation of products & water recycling will also improve other LCA criteria (natural resource depletion +110% for case D)



Possible ways of optimization



Relevant model is needed!



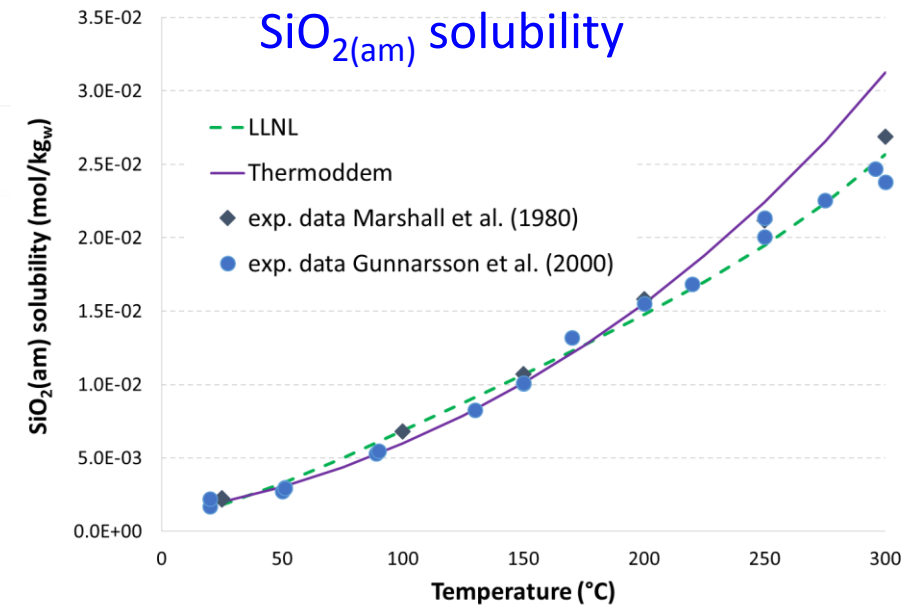
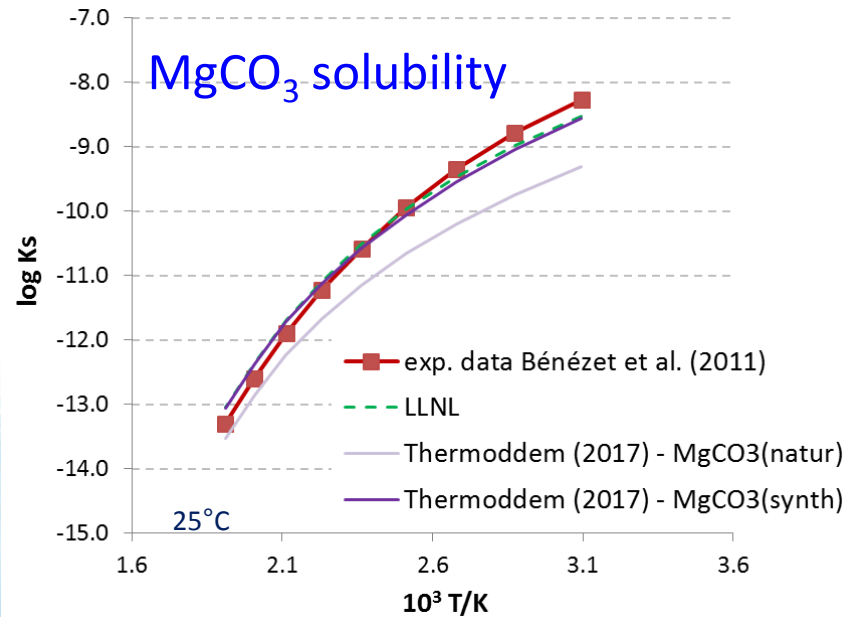


Geochemical modeling as a process design tool

Geochemical code: PHREEQC v.3 (Parkhurst & Appelo, 1999, 2013)

Available databases: LLNL, Thermoddem

Selection based on existing exp. data for main system components

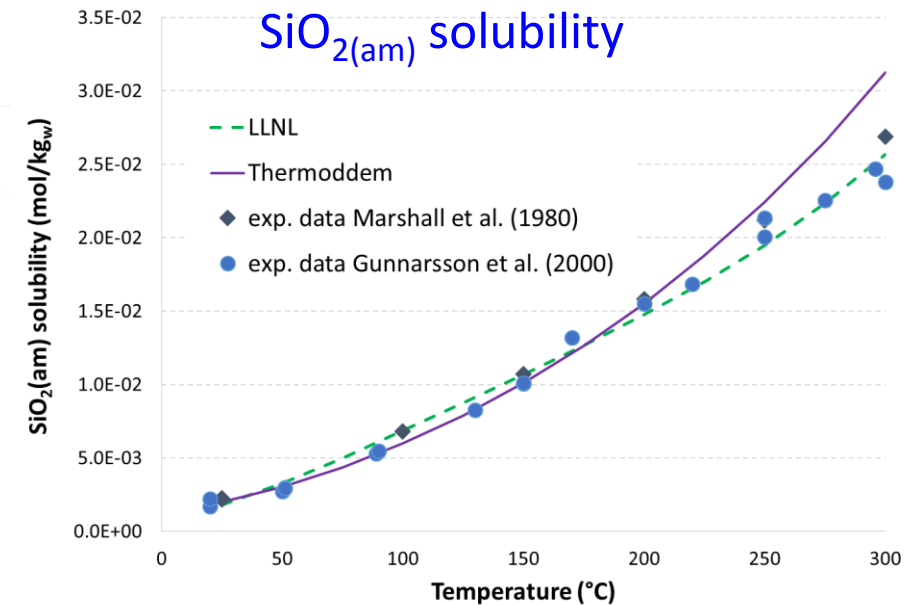
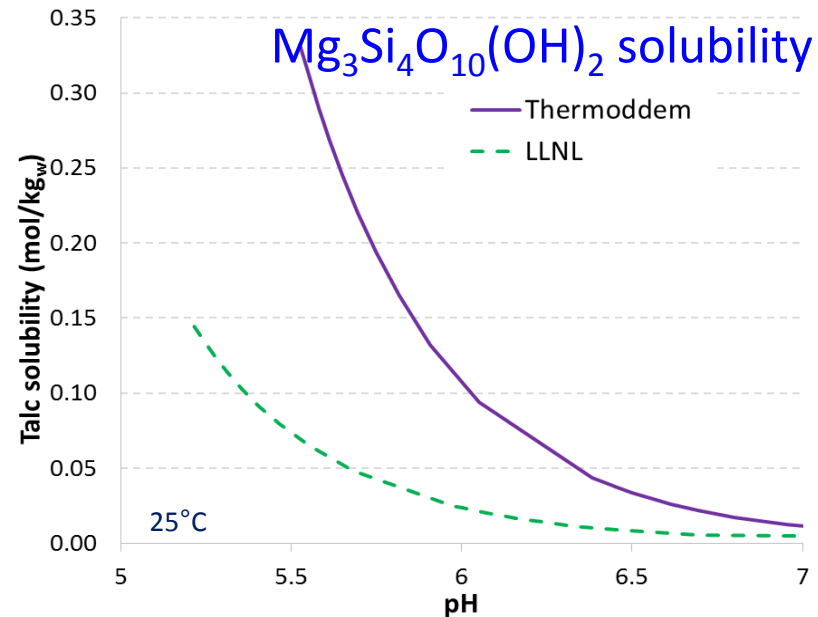


Geochemical modeling as a process design tool

Geochemical code: **PHREEQC v.3** (Parkhurst & Appelo, 1999, 2013)

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*Selection based on existing exp. data
for main system components*



Discrepancies for talc, but no solubility data available (in similar conditions) → assessment on carbonation results

Liquid: extended Debye-Hückel activity coefficient model (low salinity)

Gas: Peng-Robinson equation of state (non-ideal behavior of CO₂ - H₂O mixture at investigated P)

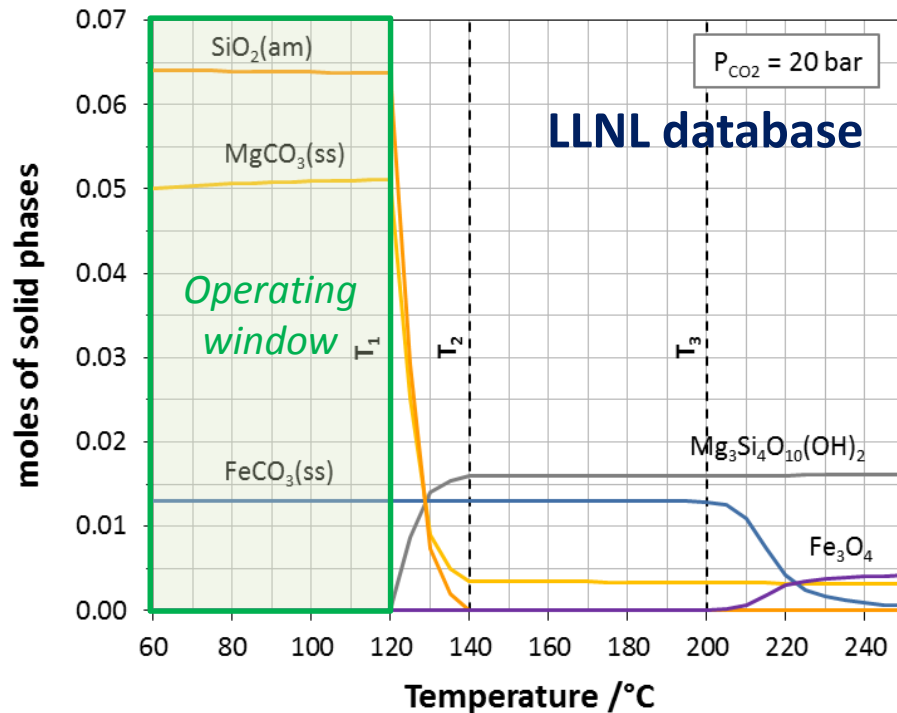
Solid: description of several **solid solutions** (e.g. (Mg,Fe)CO₃)

Case study 1: KNS / “inert” grinding medium

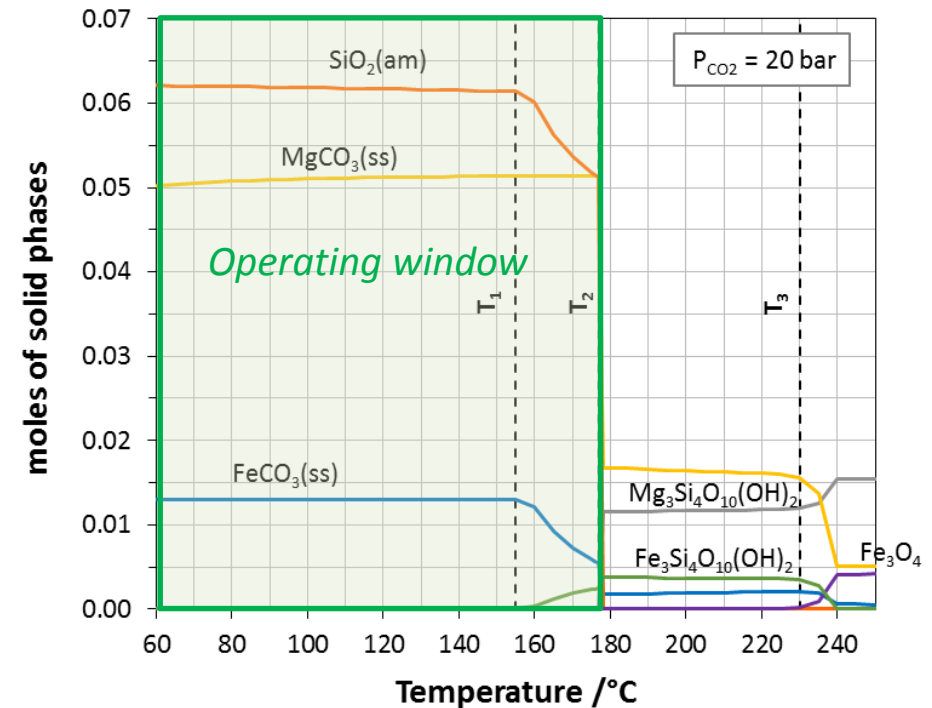
“KNS” (90 g/L) described as an assemblage of MgO, SiO₂ and FeO

All minerals including Mg, Si or Fe are allowed to precipitate, except quartz

Mineral speciation of KNS-H₂O-CO₂



Thermoddem 2017 database



➤ Threshold T for quantitative carbonation at 20 bar CO₂ depends on the database!

➤ At T = 180°C and P_{CO2} = 20 bar:

~~LLNL → theoretical max carbonation yield: 25%~~

Thermoddem 2017 → conditions close to the drop in carbonation yield

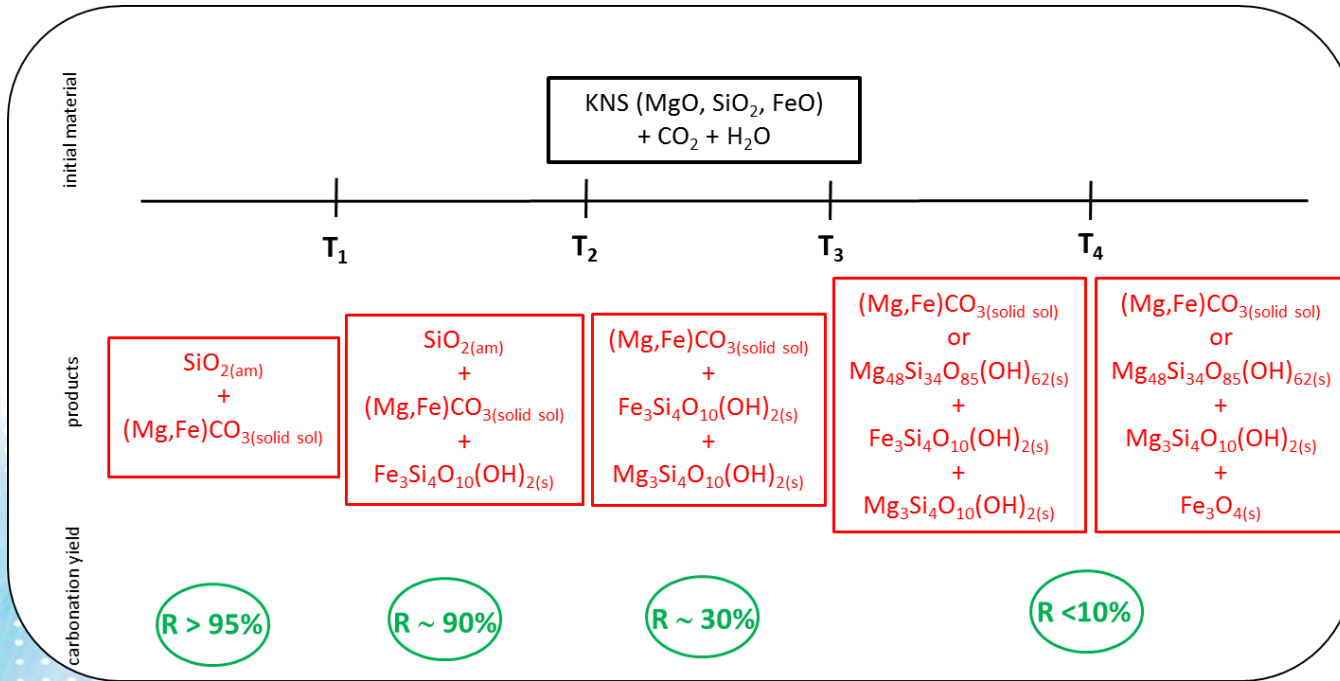


Case study 1: KNS / “inert” grinding medium

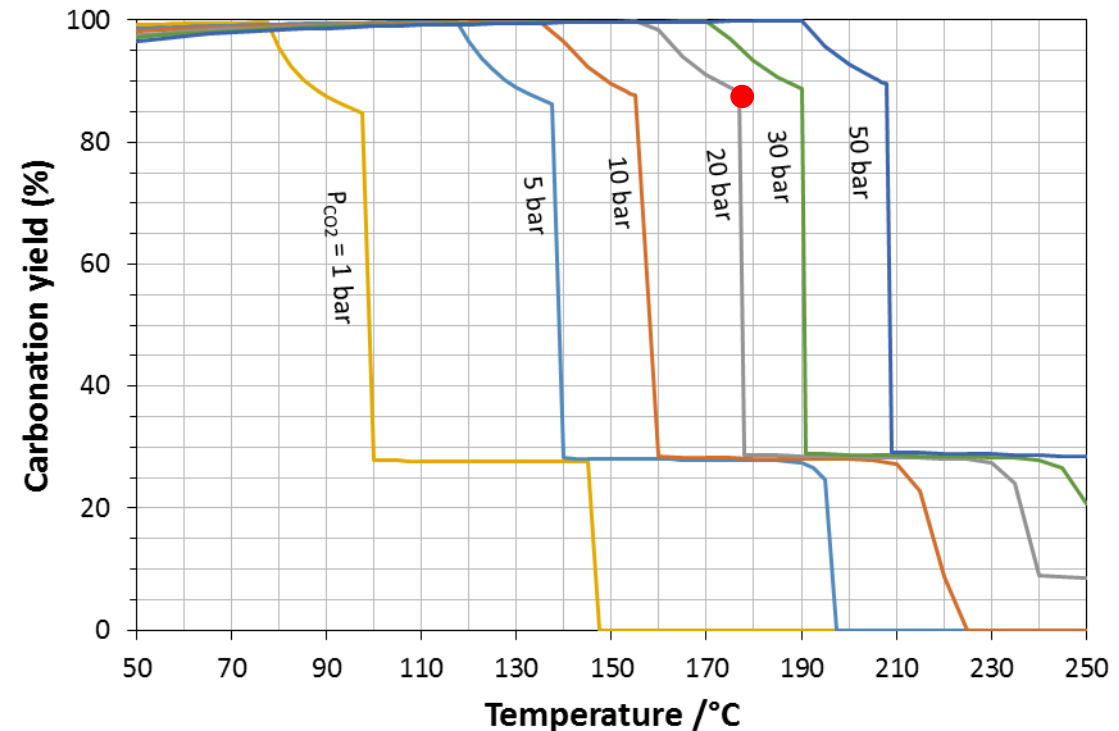
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Thermodem 2017



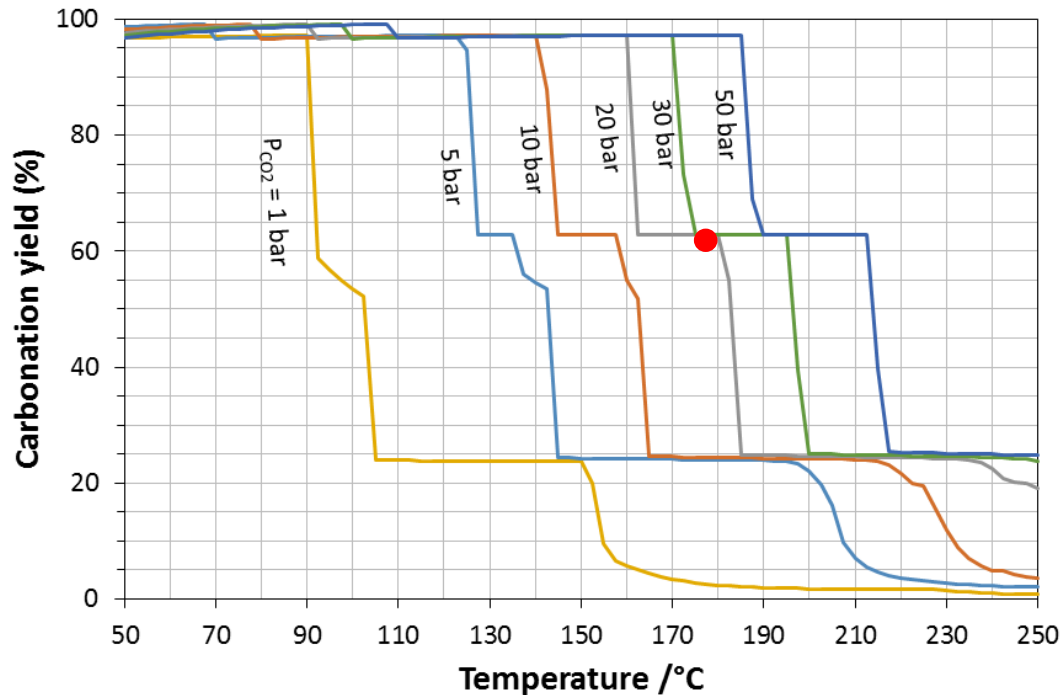
➤ Operating threshold temperature depends on P_{CO₂}



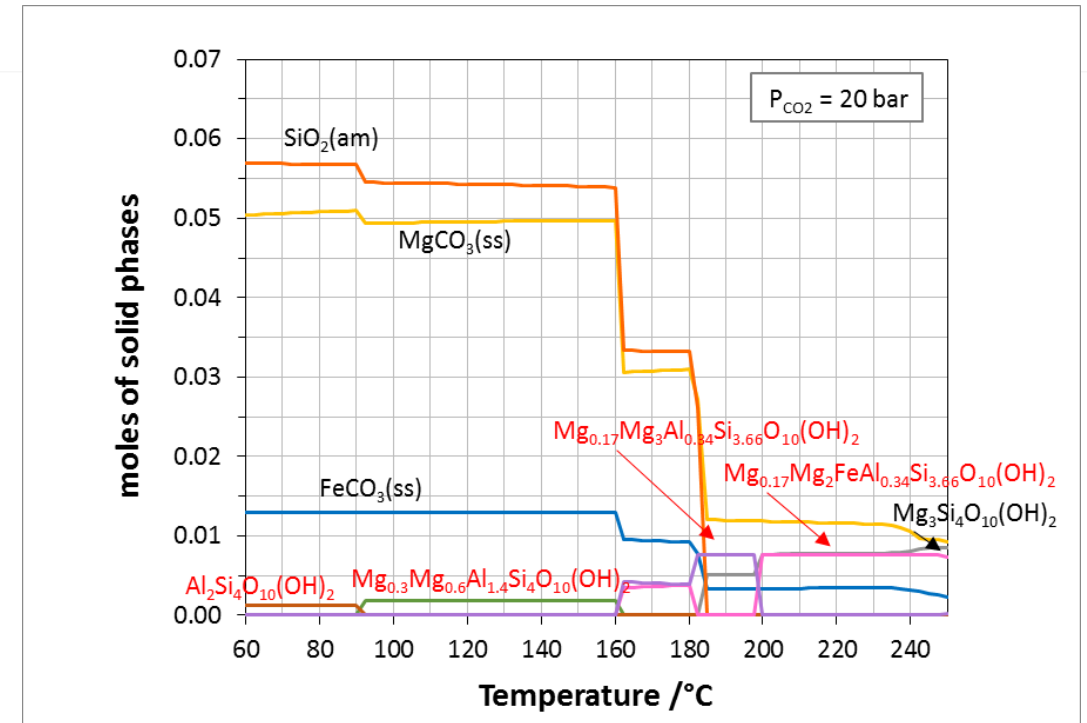
Case study 1: KNS / “inert” grinding medium

“KNS” (90 g/L) described as an assemblage of MgO, SiO₂, FeO, CaO, Al₂O₃ and MnO
 All minerals including Mg, Si, Fe, **Ca, Al or Mn** allowed to precipitate (except quartz)

Mineral speciation of KNS-H₂O-CO₂



Thermodem 2017



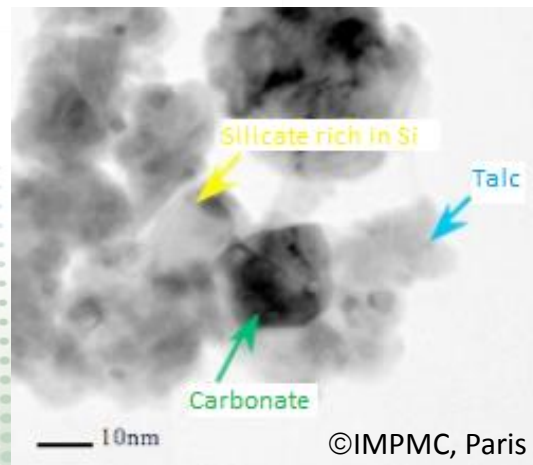
- The model predicts a noticeable effect of slag “impurities” (Al₂O₃ ~ 2%) due to the existence of various stable aluminosilicate phases



Case study 2: KNS / effect of grinding medium

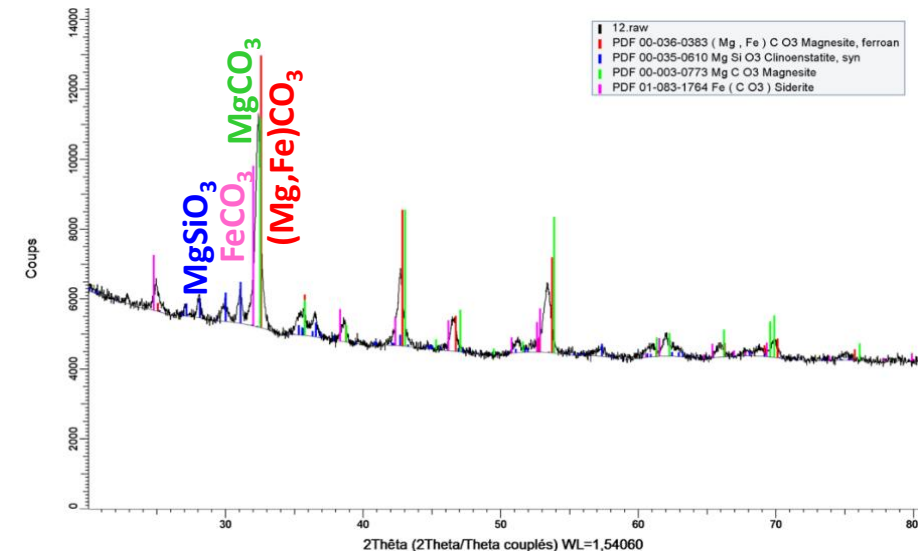
Experimental data

- Carbonation yield ~ 50% with sand (180°C, 20 bar, 90 g/L KNS)
- Crystallized phases = initial mineral phases (enstatite, ferrosilite, augite), quartz (sand) & mixed carbonates (dominated by MgCO_3 pole)
- TEM/EDX



→ Precipitation of various (amorphous) silicates

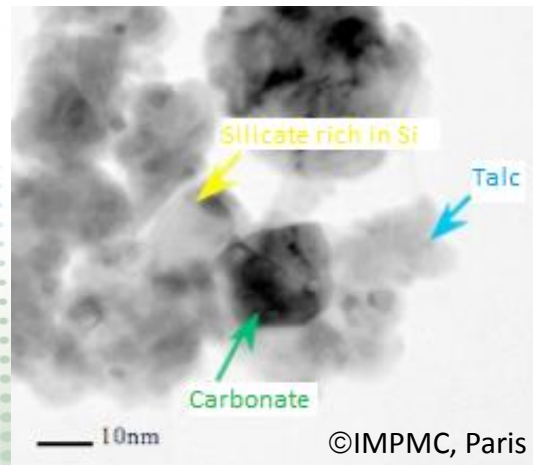
- Higher yield achieved with stainless steel beads
... but increase of Fe content in solid product &



Case study 2: KNS / effect of grinding medium

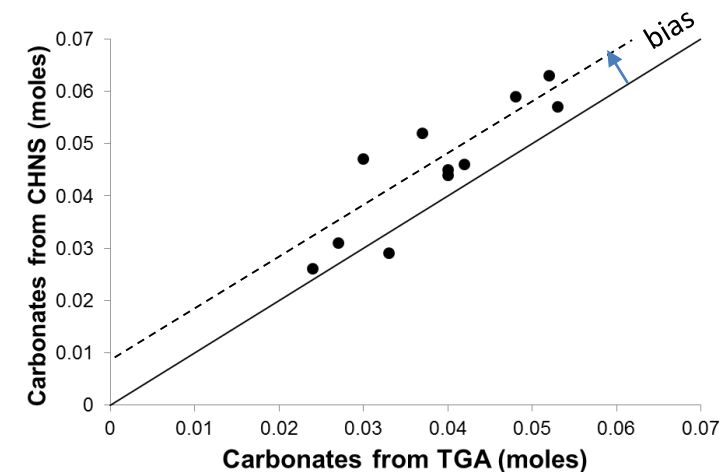
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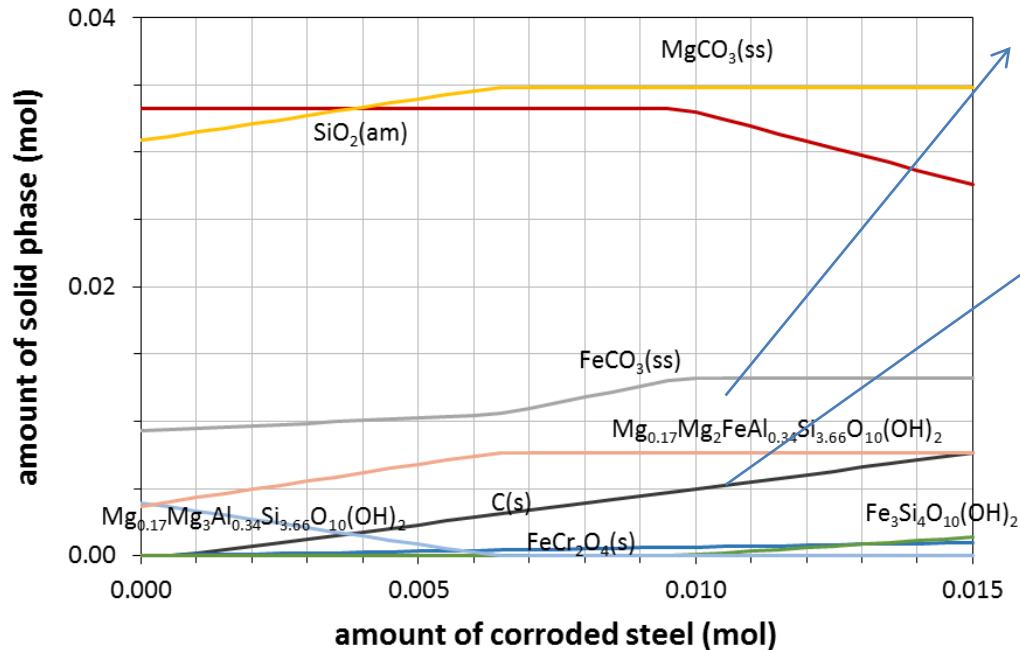
- Higher yield achieved with stainless steel beads ... but increase of Fe content in solid product & a few discrepancies between carbonate amounts calculated from TGA and carbon content



Case study 2: KNS / effect of grinding medium

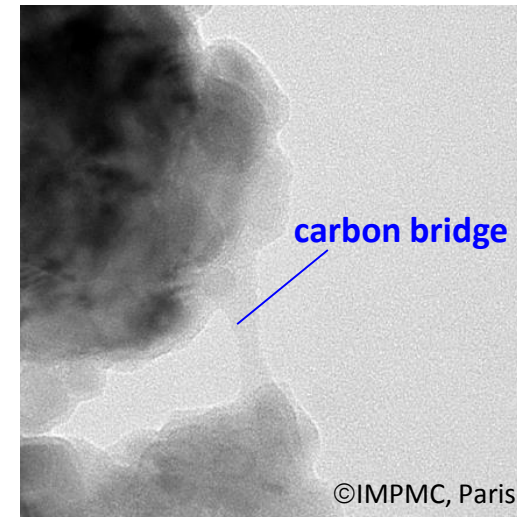
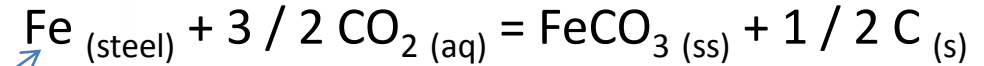
“KNS” described as an assemblage of MgO, SiO₂, FeO, CaO, Al₂O₃ and MnO
Steel beads modeled as a (Fe_{0.87}Cr_{0.13}) solid solution

Mineral speciation of KNS-H₂O-CO₂



Fe extracted from beads as FeCO₃ & ferro-magnesium-aluminosilicate

Formation of solid carbon:



$P_{\text{CO}_2} = 20 \text{ bar}, T = 175^\circ\text{C}, \text{slag conc.} = 90 \text{ g/L}$

➤ **Stainless steel beads are corroded during attrition-leaching under CO₂**

Case study 3: Batch simulation for olivine ore

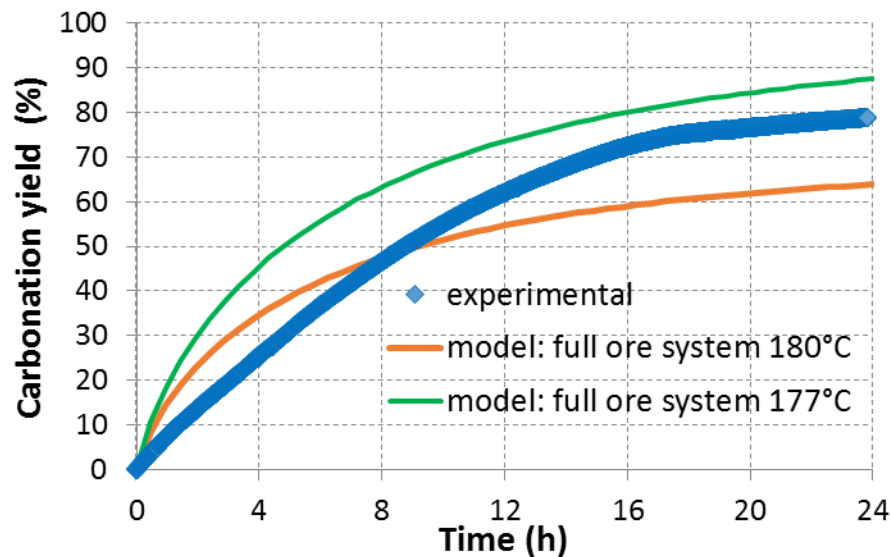
“Synthetic olivine” described as an assemblage of MgO, SiO₂, FeO, CaO, Al₂O₃ and MnO

Initial PSD accounted for, dissolution kinetic parameters from Prigiobbe et al. (2009)

Alumina beads modeled as corundum, kinetic parameters from Palandri & Kharata (2004)

Time-evolution of carbonation yield

“Inert” grinding medium



$P_{CO_2} = 20 \text{ bar}$, $T = 180^\circ\text{C}$, ore conc. = 90 g/L

Effect of alumina grinding beads

Very slow dissolution kinetics

→ Negligible effect on system speciation

- Good agreement between experimental data and modeling
- **Process dynamics driven by the dissolution rate of fresh ore surface**



Learnings & issues

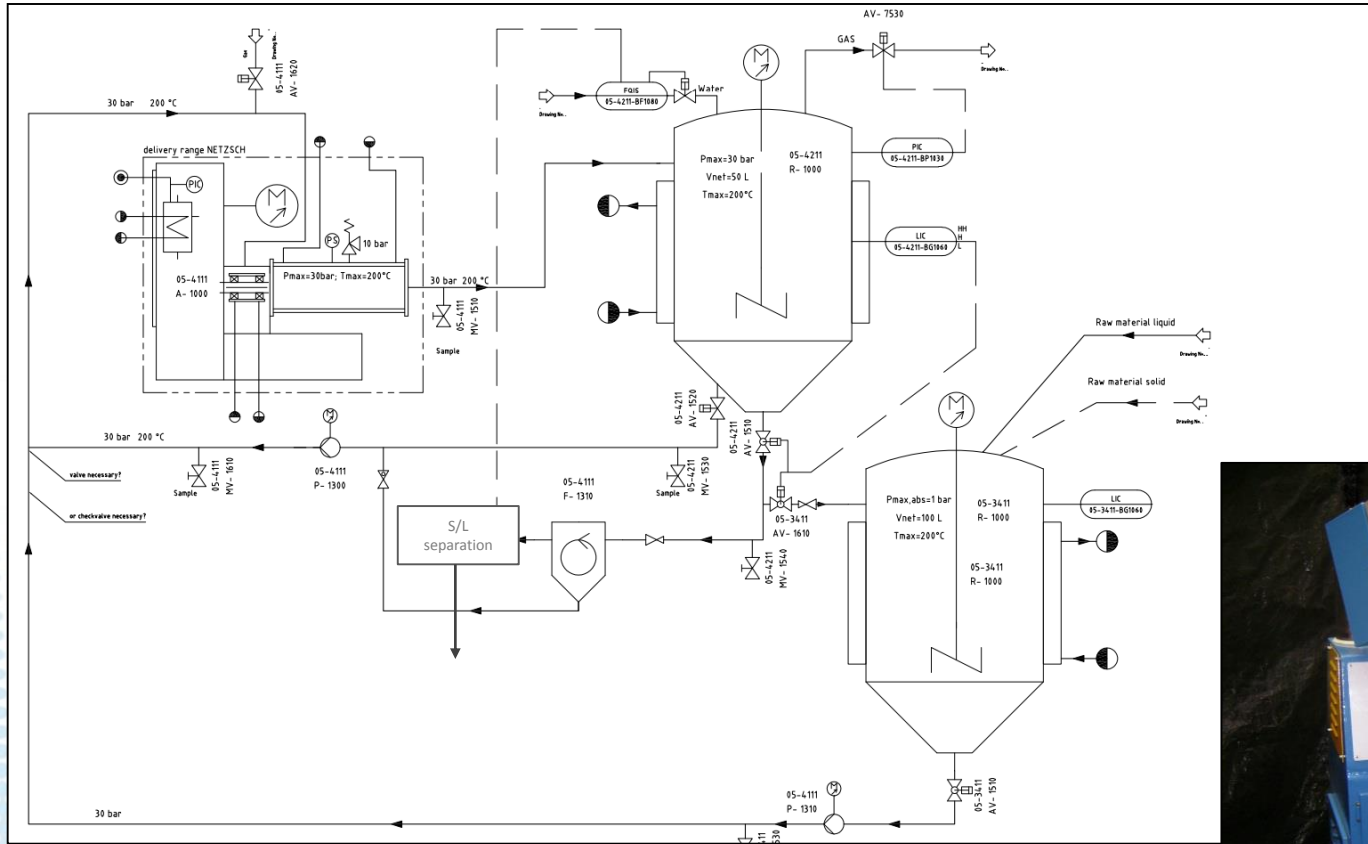
- Proof of concept of the attrition-carbonation process with a stirred bead mill; **Synergy between attrition & carbonation**
- **Favorable LCA**; several optimization levers to improve process efficiency, cost & environmental impact
- **Grinding medium to be carefully selected (autogenous mode?)**
- **Geochemical modeling is a powerful tool** for designing the attrition-carbonation process:
 - *equilibrium calculations* → suitable operating window (to be verified experimentally) & material selection for the process equipment (grinding media)
 - *coupling of thermodynamics with chemical kinetics* → process sizing & optimization

SO WHAT'S NEXT ?

- **A continuous scalable demonstrator**
- **Beneficiation of carbonation products**



Continuous bench-scale process



Attrition reactor ~4 L operating under T (max 200°C) & P (max 30 bar)



<http://www.isamill.com>

➔ **Bench-scale pilot reactor to be built in the coming months**



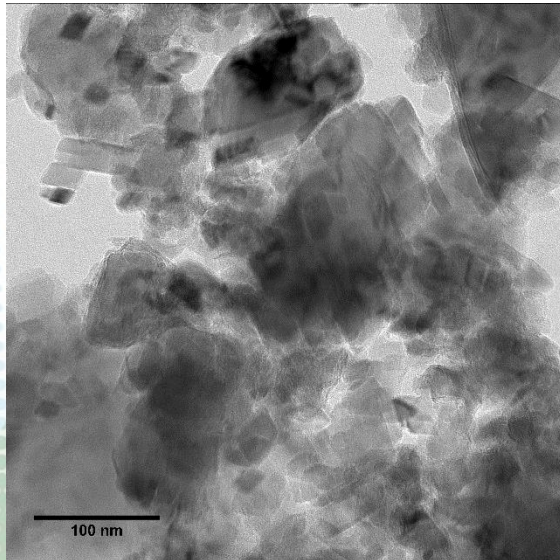


Utilization of MC products as construction or filling materials

➤ could in theory absorb Gt of CO₂ (approximately 33 billion tons of concrete produced / year)

Hybrid process products:

agglomerates of nano-sized particles of carbonates, silica & silicates



almost "as it is"

after heating

✓ Potentially highly reactive additives

Inert filler or pozzolana
(mainly ultra-fine silica fraction
+ MgCO₃)
CO₂ sequestered (& avoided)

Hydraulic binder
(mainly Mg rich fraction
+ SiO₂)
CO₂ avoided



Goal: valorization without solid separation & with minimum dewatering

- ✓ Virtuous CO₂ loop
- ✓ Reduction of natural resource depletion (no need for limestone)
- ✓ Reduction of heat demand (T_{calcination} ↓)
- ✓ Local production of construction materials



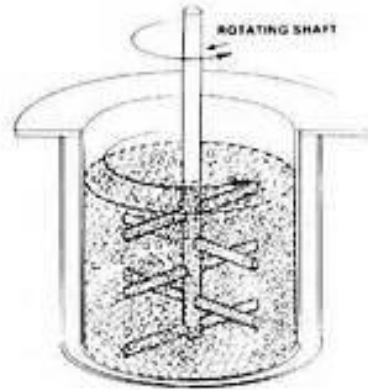


New concept: CCUS combined with Enhanced Metal Recovery

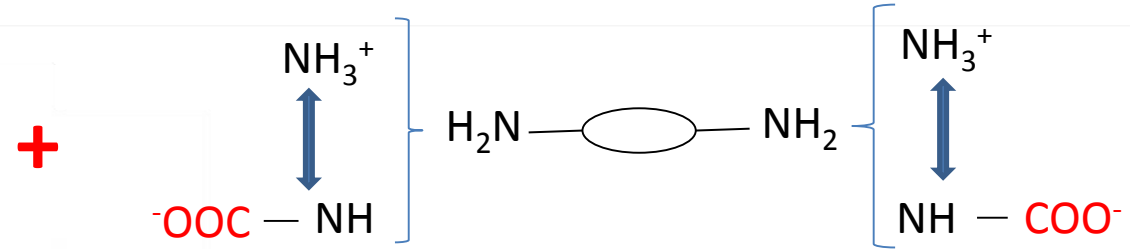
Innovative chemistry under attrition environment

Attrition-carbonation process

CO₂
→
→
(Ni) slags



Polyamines



efficient CO₂ capture (dilute flue gases)

+ catalysis of CO₂ mineralization

+ potential modulation of silica precipitation

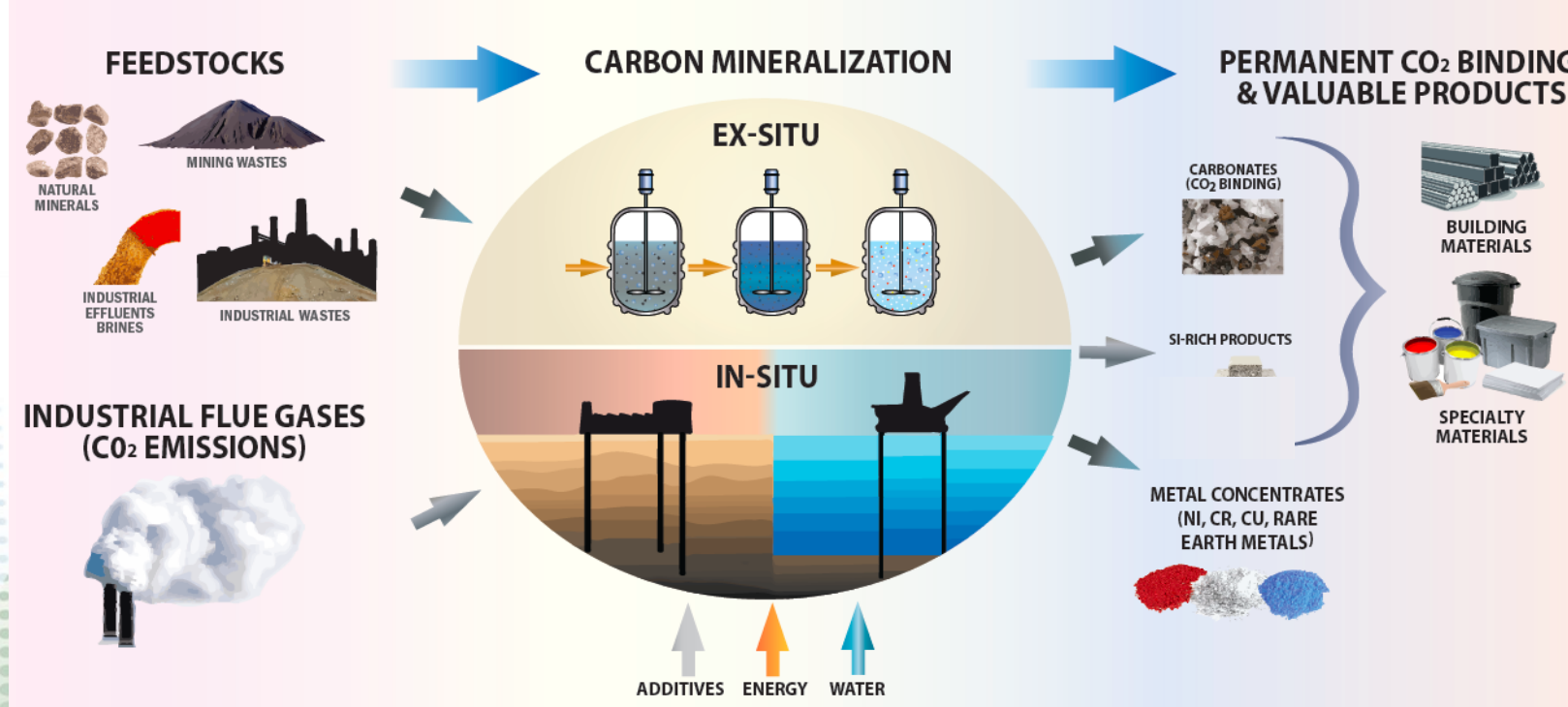
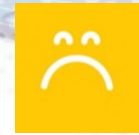
+ selective metal recovery



Overall scheme for CO₂ mineralization

"Historically", CO₂ mineralization was compared to geological storage, in terms of storage cost and avoided CO₂:

Limited development ...



Mission Innovation, CCUS* Workshop, Houston, Sept. 2017; <http://mission-innovation.net/our-work/innovation-challenges>

In recent years, the mineralization of CO₂ systematically combines CO₂ storage and production of commercial goods, coupling environment and economy:

Booming development!





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J. Leclaire & J. Septavaux (**ICBMS Villeurbanne**)
for their valuable contribution



Thank you for your kind attention!



The actual team



France Bailly, Director



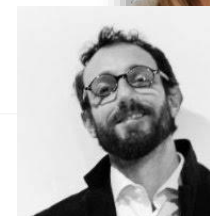
Pr. Florent Bourgeois



Dr. Carine Julcour



Dr. Laurent Cassayre



Pr. Julien Leclaire



Dr. Solène Touzé



Pr. Martin Cyr



