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

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6th Accelerated Carbonation for Environmental and Material Engineering Conference, March 11-14, 2018, Newcastle, New South Wales, Australia

LGC

CARMEX

French National Research Agency
(ANR CO_2 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“
(2015-2016)

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

CARBOSCORIES II

Caledonian Energy Agency
(2018-2021)

Bench-scale continuous pilot
Valorisation route for MC products

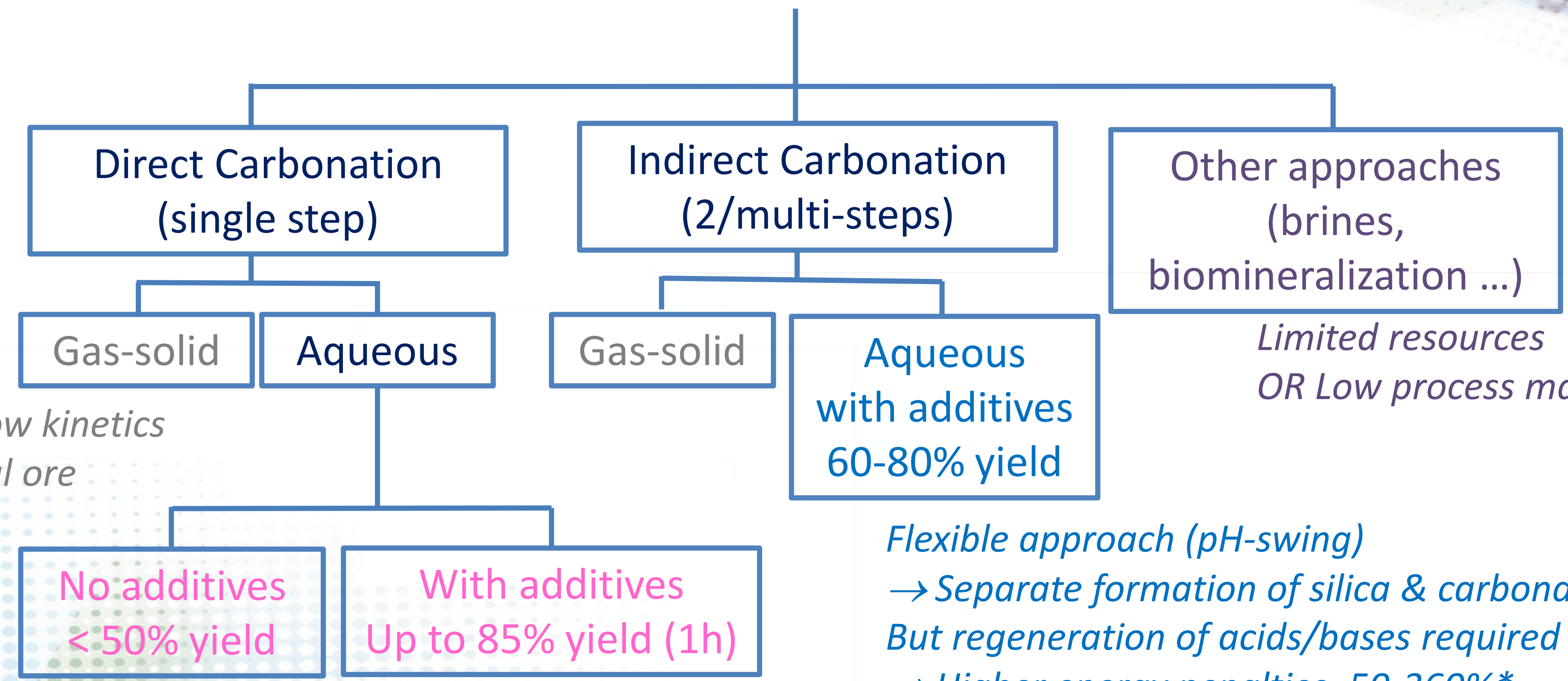
CO_2EMR

Collaborative work

CO_2 Enhanced Metal Recovery

LGC

Ex-situ Mineral Carbonation pathways



High T, slow kinetics
for natural ore

Limited resources
OR Low process maturity

Flexible approach (pH-swing)
→ Separate formation of silica & carbonates
But regeneration of acids/bases required
*→ Higher energy penalties: 50-360%**

Not so simple an approach
Valorisation routes required for solid mixture (M traces?)
*Net energy penalties: 50-220%**

Adapted from *Sanna et al. (2014)*

*based on < 2010 literature routes for 154 MWe coal-fired power plant producing 1Mt-CO_2/yr

CNRS
Université de Toulouse

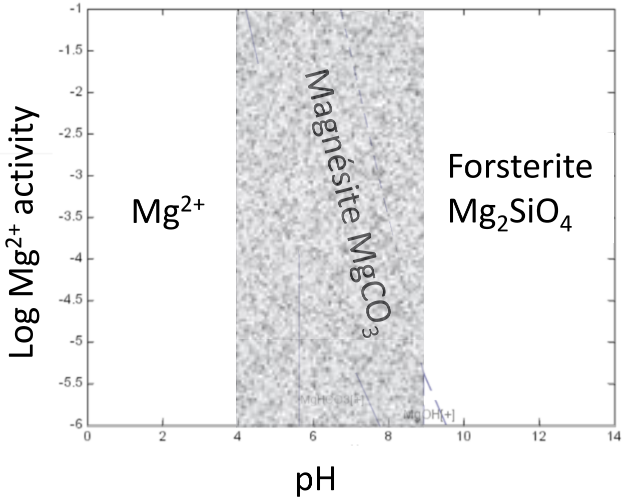
Studied MC pathways

Direct Carbonation (single step)

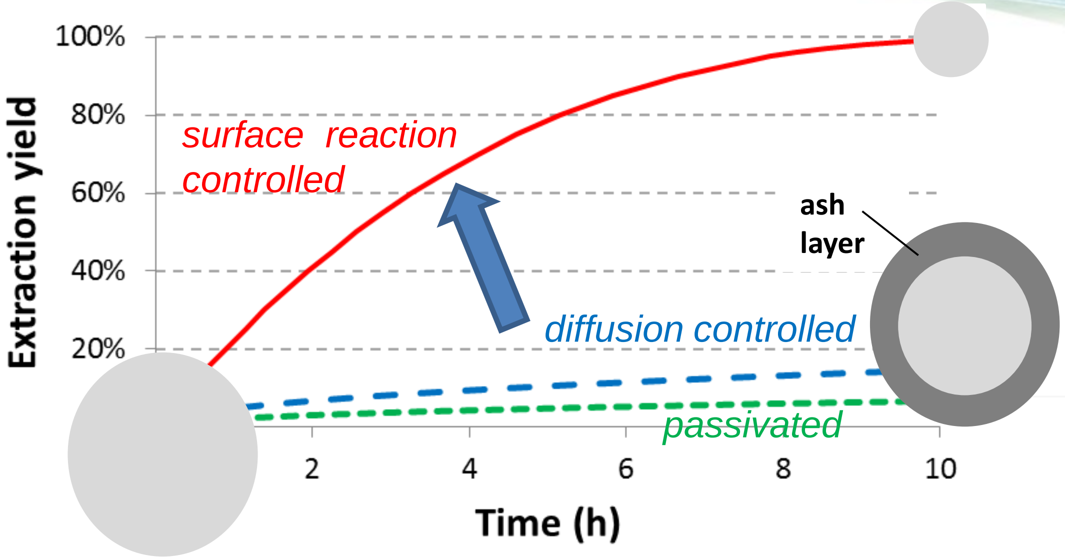
Aqueous

No additives < 50% yield

With additives Up to 85% yield (1h)

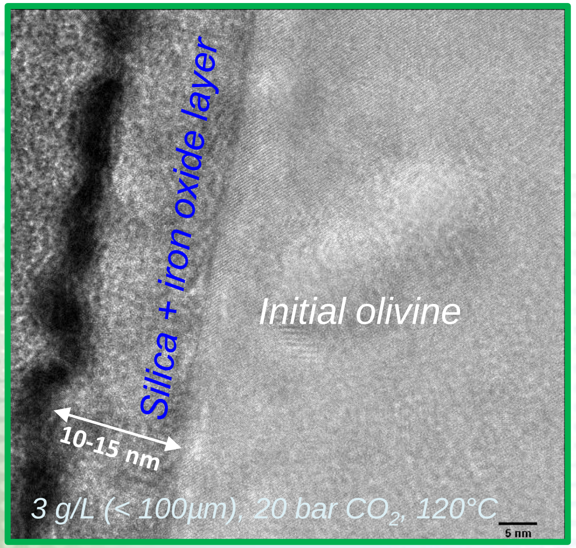


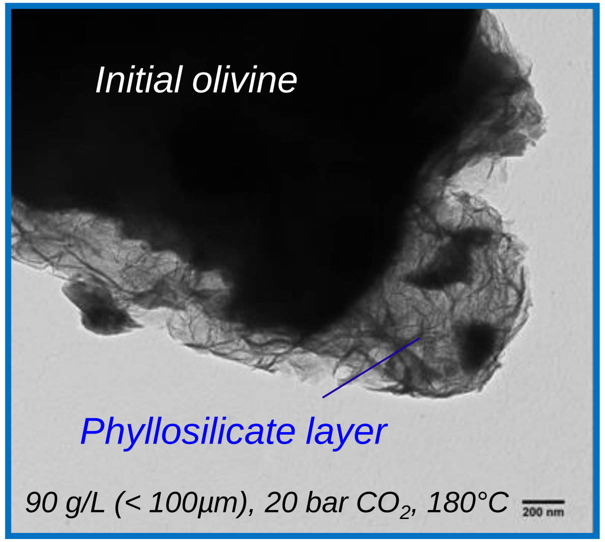
Surface leach layer & mechanisms



Passivating

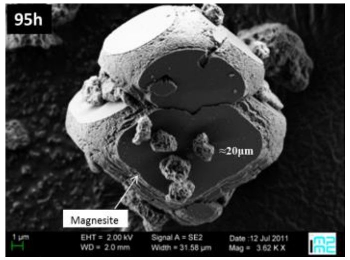
→ No carbonate





Diffusion controlling

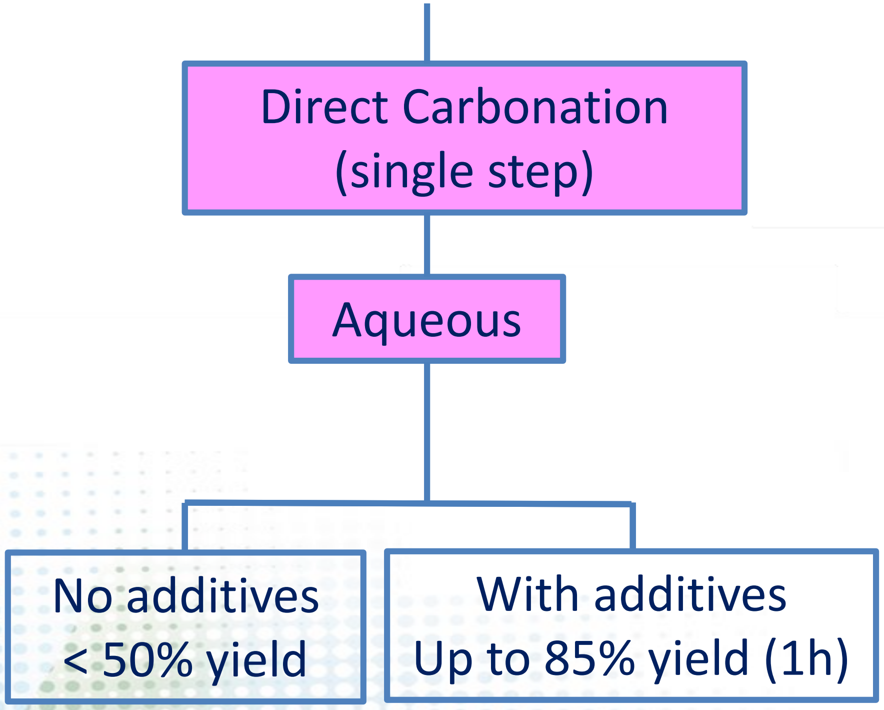
Carbonation yield
< 10% (90 g/L, 95 h)



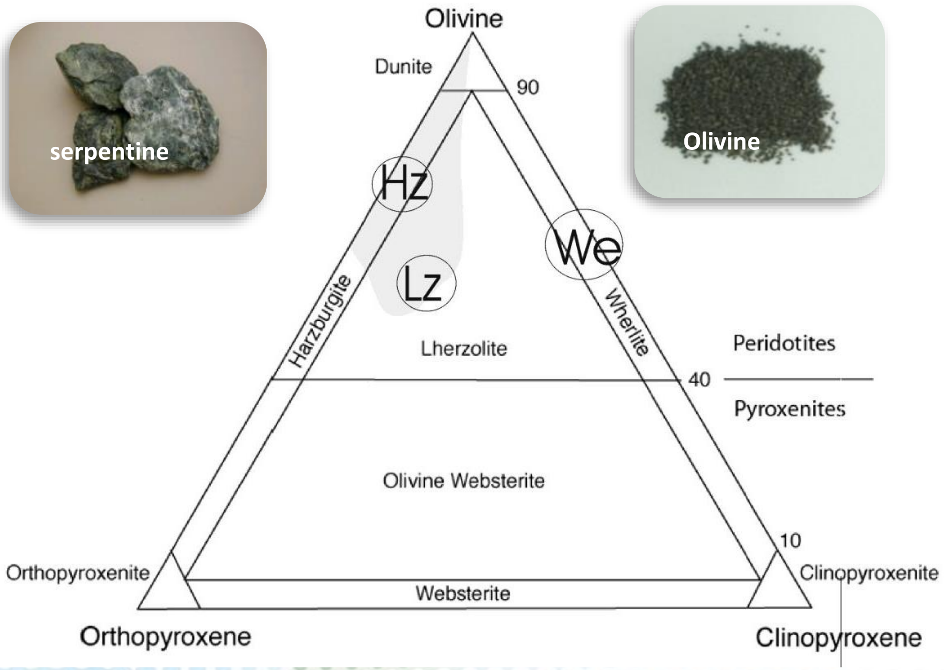
FIB cross-sections of olivine particle after leaching (TEM) ***(Bodenan et al., 2014)***

EXPERIMENTAL METHODOLOGY

Studied MC pathways



Ores



Bodenan et al. (2014)

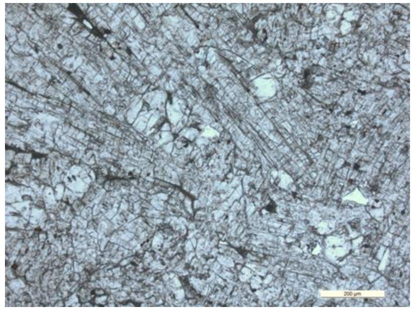
Serpentinisation degree up to 90%

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)

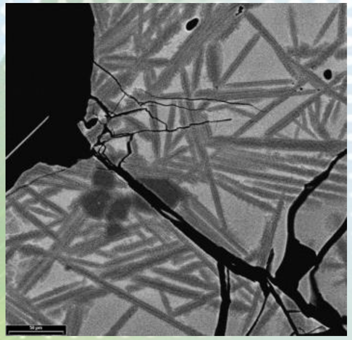
$30.8 < MgO < 47.4\%$, $39.3 < SiO_2 < 46.3\%$, $7.3 < Fe_2O_{3tot} < 9.8\%$, $0.2 < CaO < 5.0\%$, $0.2 < Al_2O_3 < 4.0\%$

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



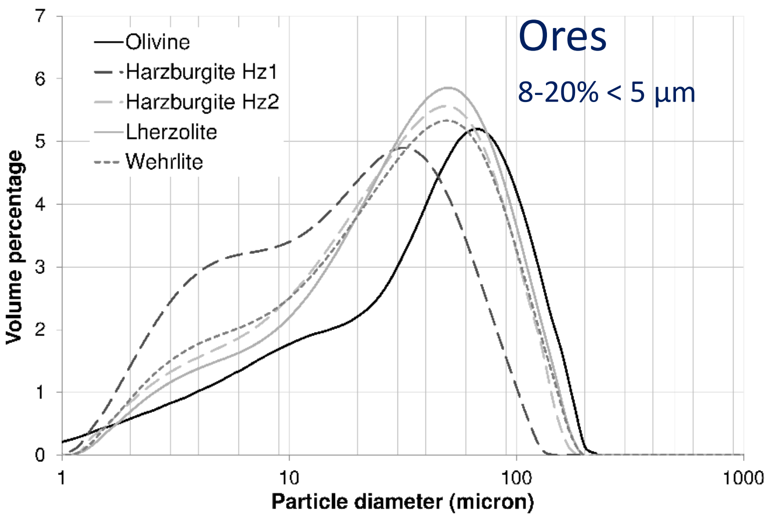
$MgO \sim 30\%$, $SiO_2 \sim 52\%$, $Fe_2O_{3tot} \sim 13\%$,
$CaO < 0.5\%$, $Al_2O_3 \sim 2\%$

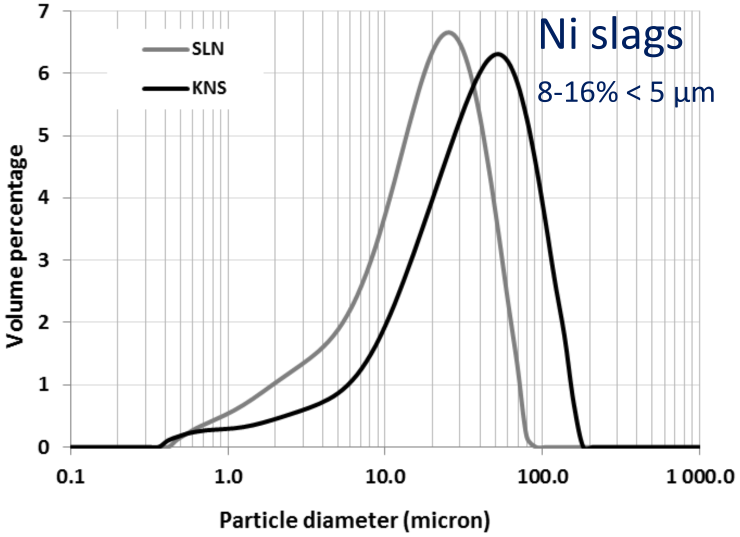
Solid preparation

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

- **Mechanical sampling**

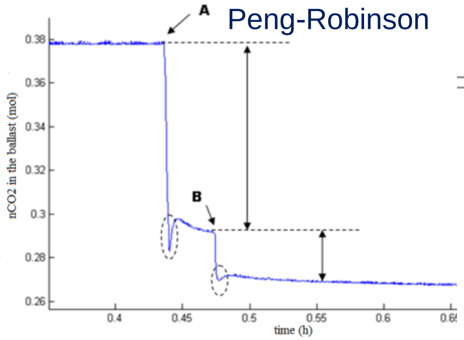
- **Initial particle size distribution**

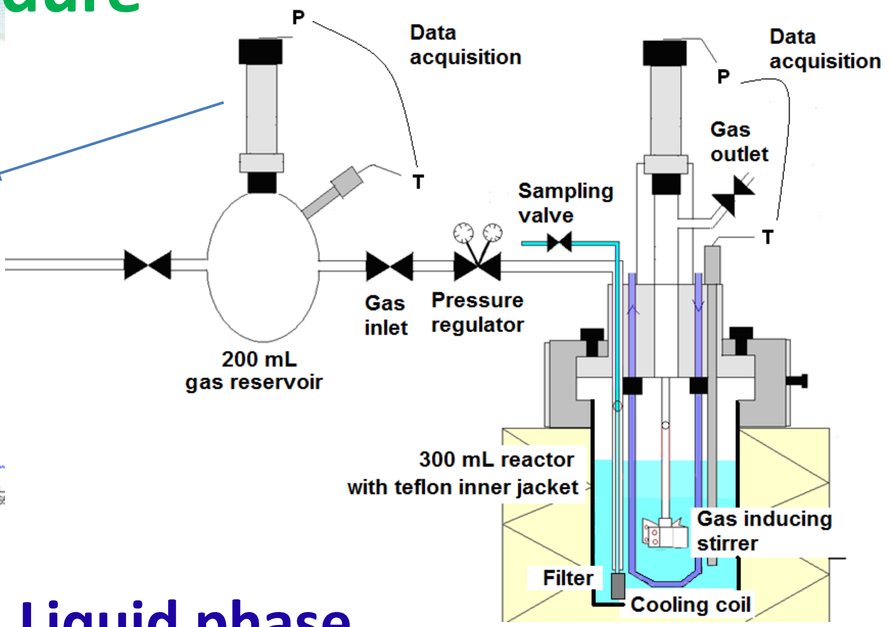




Carbonation set-up & procedure

- 300 mL autoclave reactor
- Controlled atmosphere (P_{CO2}) and T
- Gas auto-dispersing stirrer (800 rpm)
- Continuous recording of CO_2 consumption (24 h)

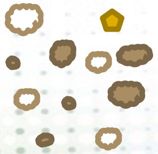


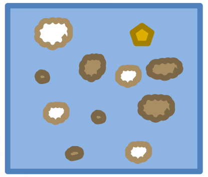


Laser diffraction analysis
Filtration (0.2 µm)

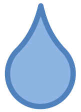
Solid phase

drying (70°C)





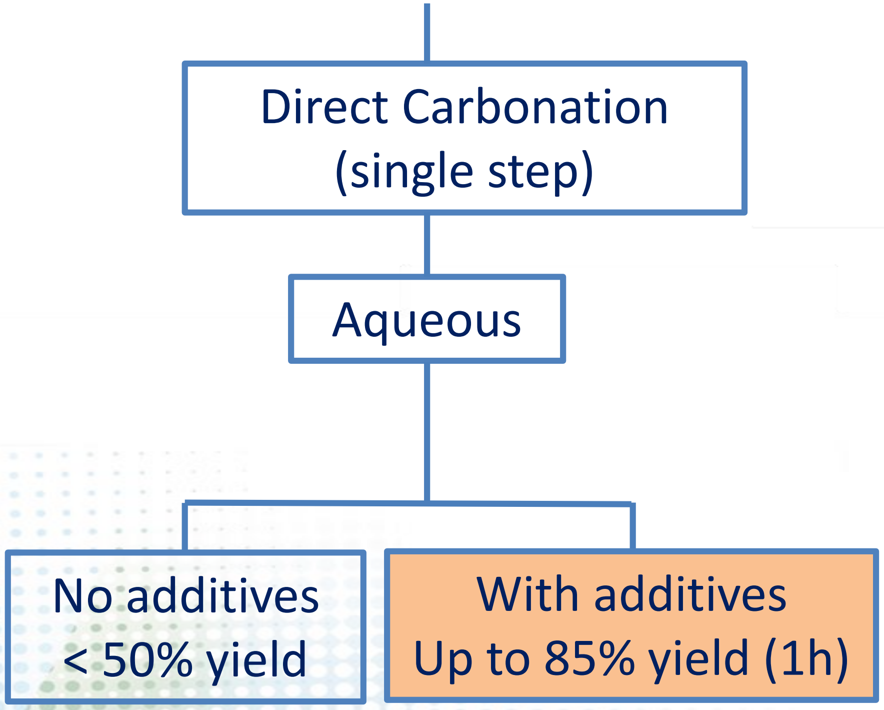
Liquid phase



- 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

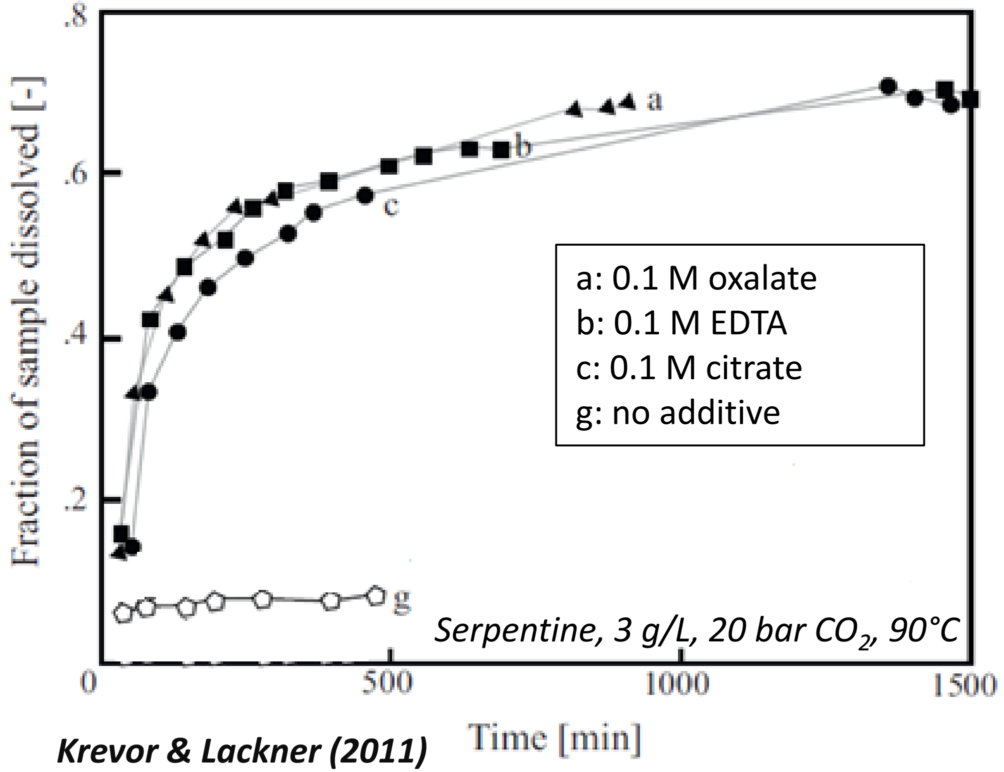


CHELATING AGENT APPROACH

LGC

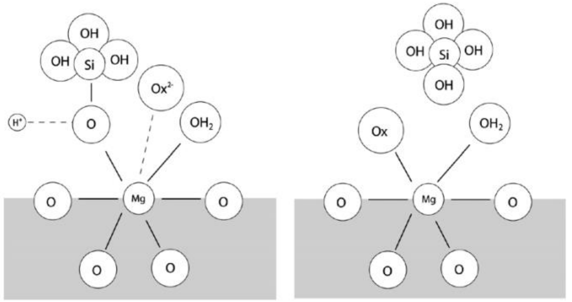
State of the art

➢ Effect of organic polyacids on dissolution rate



Krevor & Lackner (2011)

➢ 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)

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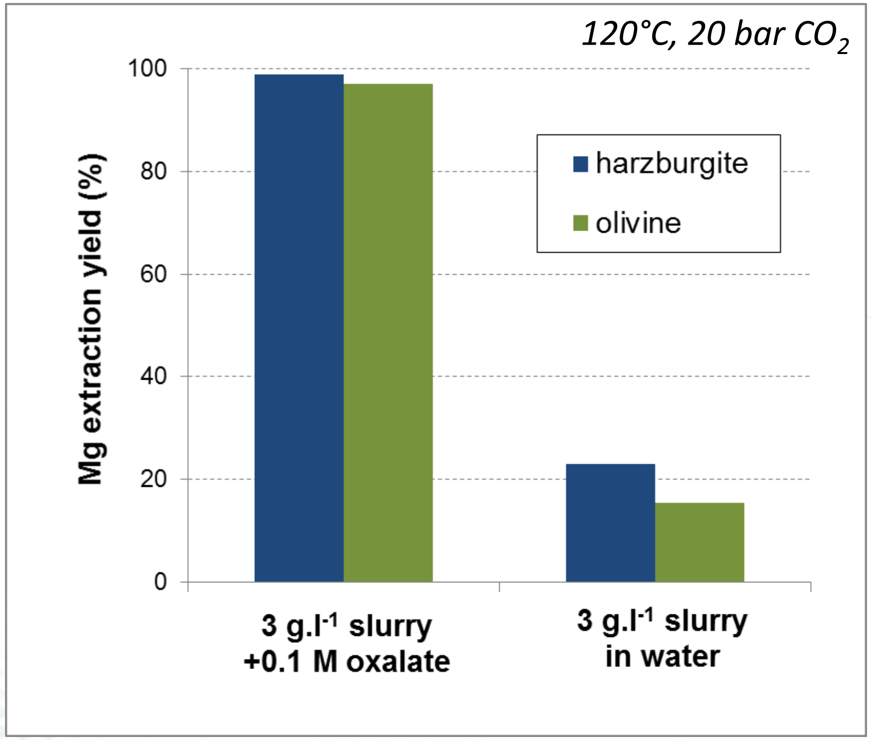
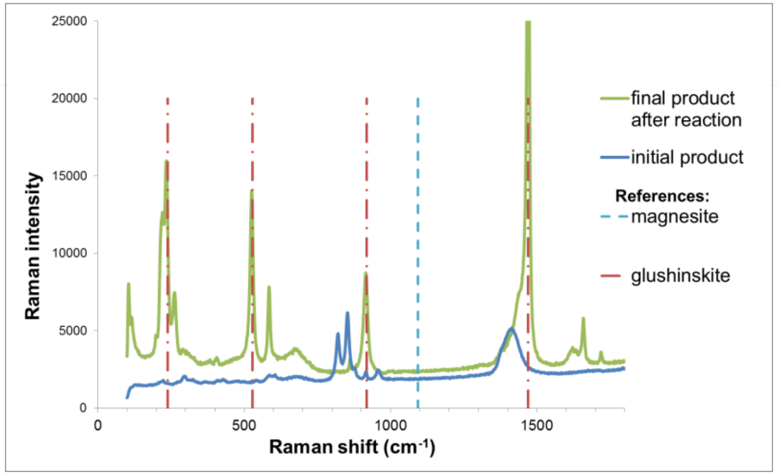
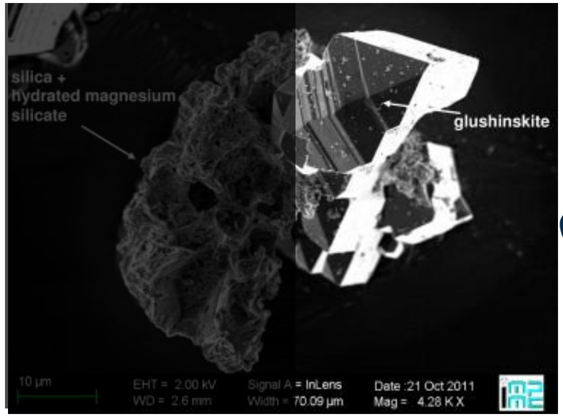
Oxalate-enhanced dissolution of olivine: leaching yield & Mg speciation





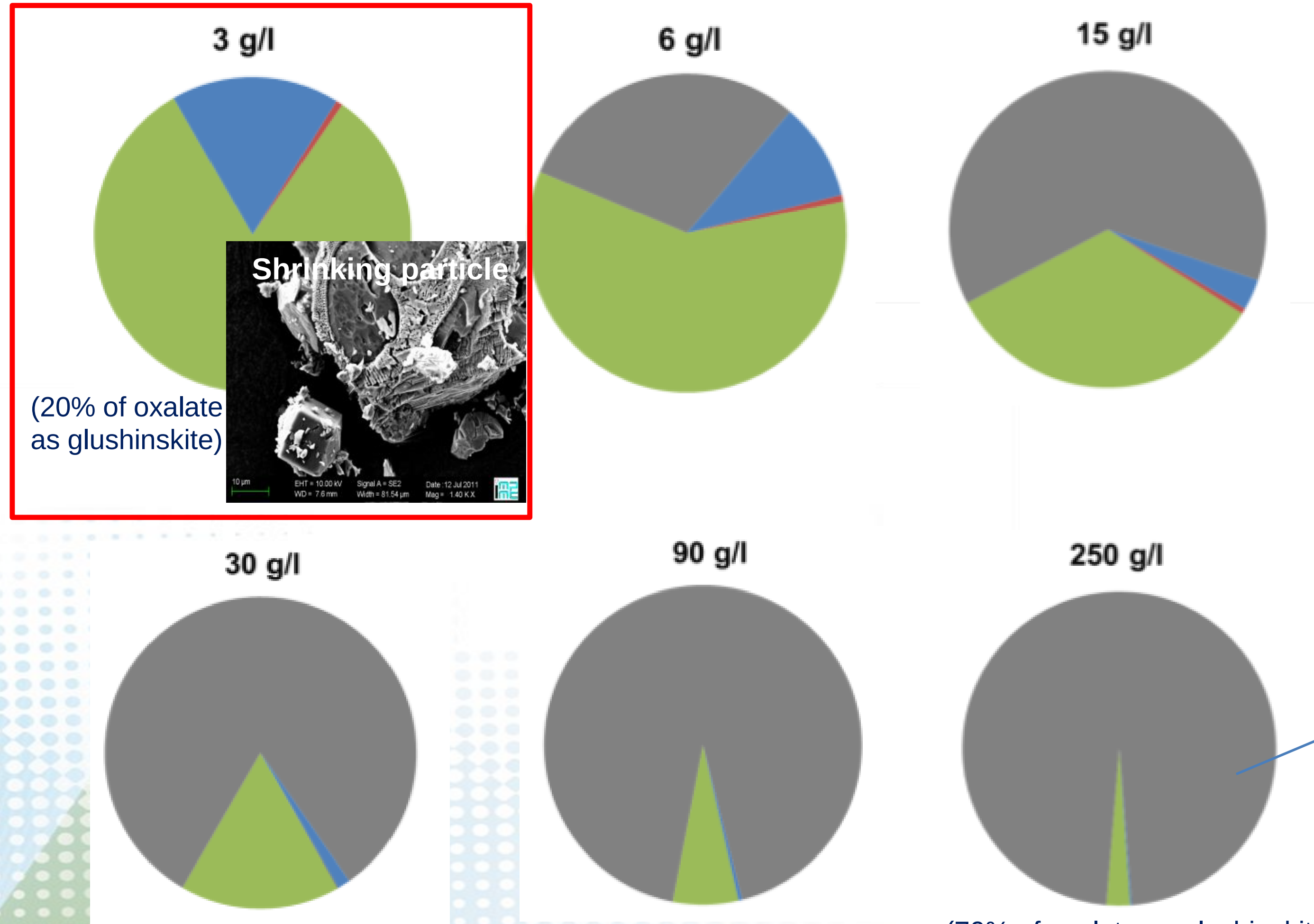


- ➢ Significantly improved extraction yield with oxalate at 3 g/L, but formation of solid by-product: **glushinskite** ($MgC_2O_4.2H_2O$)

- ➢ Any compromise between glushinskite precipitation & Mg carbonation?

LGC

Oxalate-enhanced dissolution of olivine: effect of slurry concentration



(70% of oxalate as glushinskite)

Mg speciation after 24h

120°C, 20 bar CO_2, olivine < 100 µm, speciation after cooling

- Carbonates
- Glushinskite
- Olivine
- Solution

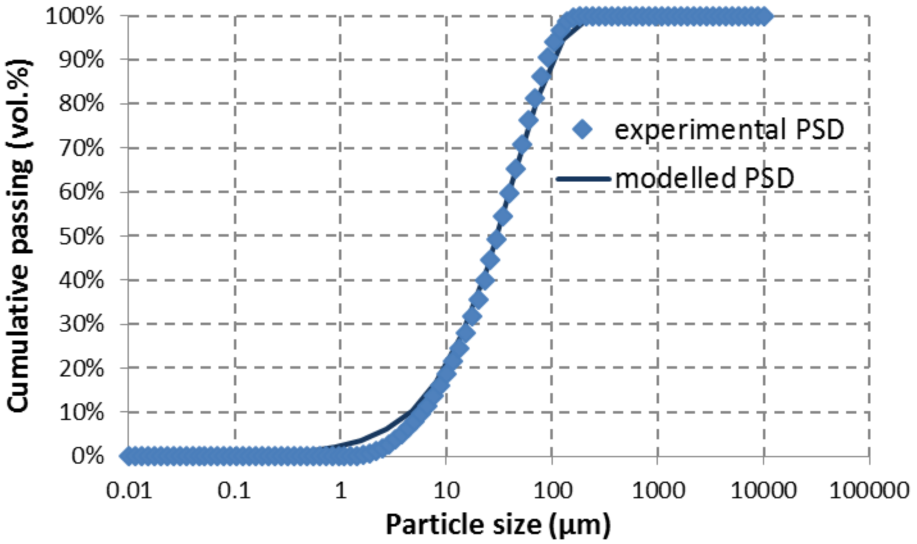
➢ Carbonation yield < 1% → not a viable option in these conditions

➢ Could geochemical modeling predict such competing effects?

Oxalate-enhanced dissolution of olivine: kinetic modeling

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

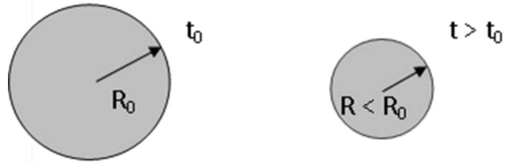
~20 size classes (SSA_{0i}, m_{0i}) generated from Rosin Rammler PSD model



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

Shrinking particle model

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



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

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

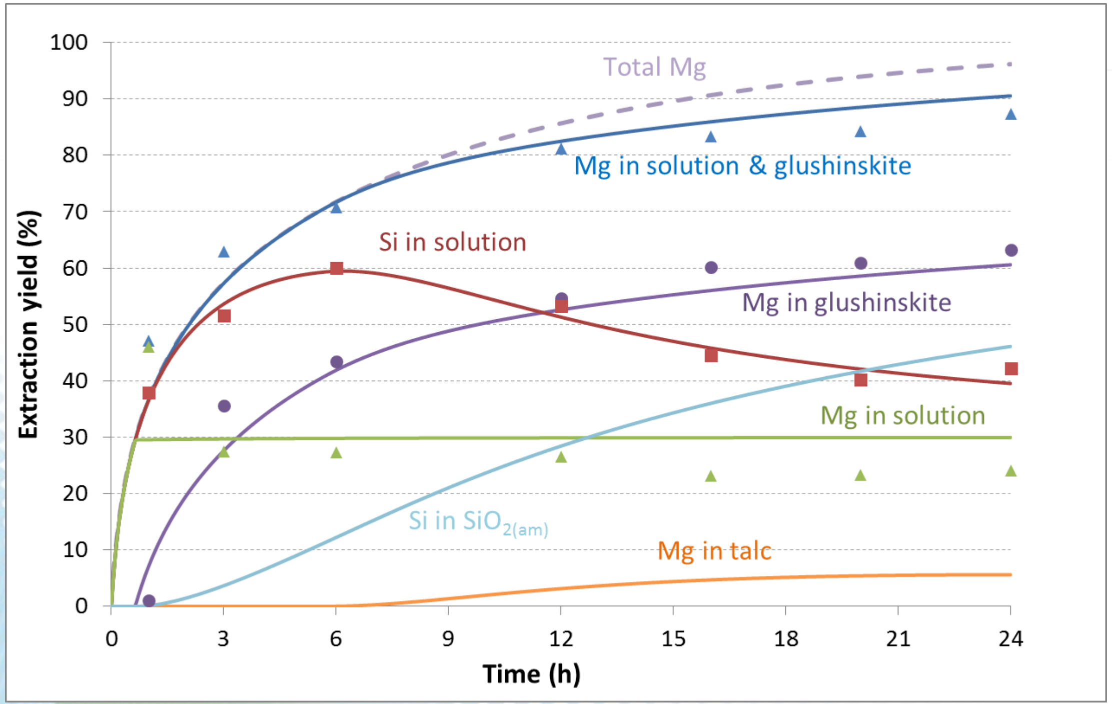
surface reaction rate from Prigiobbe & Mazzotti (2011)

LGC

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

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)

120°C, 20 bar CO_2,
3 g/L olivine < 100 µm

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

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

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

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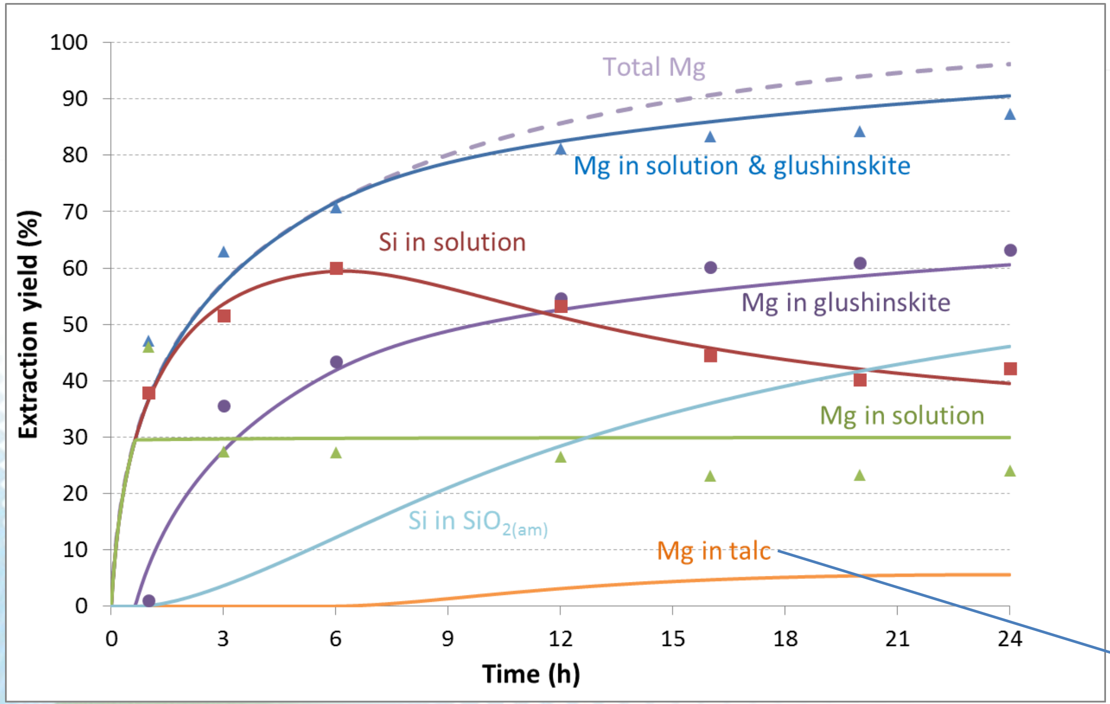
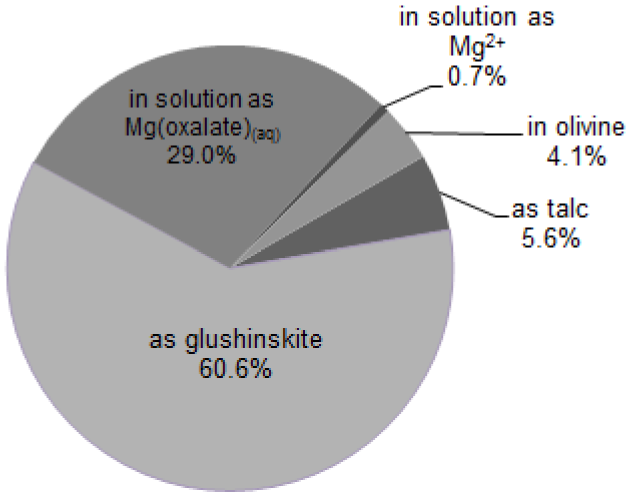
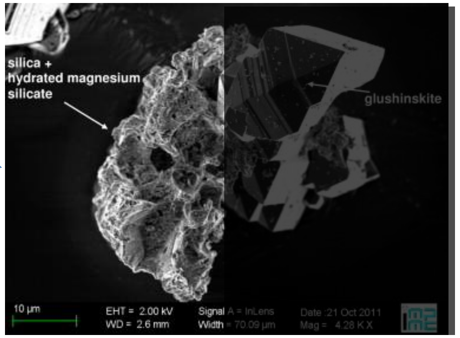


Bonfils et al. (2012)



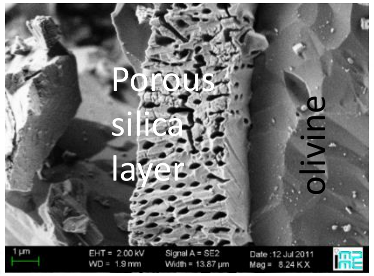


➢ Good agreement with experimental data at 3 g/L
→ chemical controlled reaction

Learnings & issues

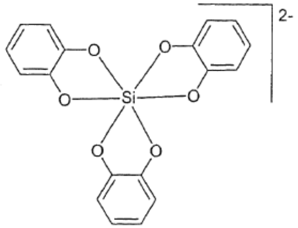
- Organic polyacid salts (oxalate, citrate, EDTA): too strong Mg binders for MC at moderate P_{CO2}
- Alternative option: silica(te) layer modulation / impeding by ligands

Oxalate



Catechol

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



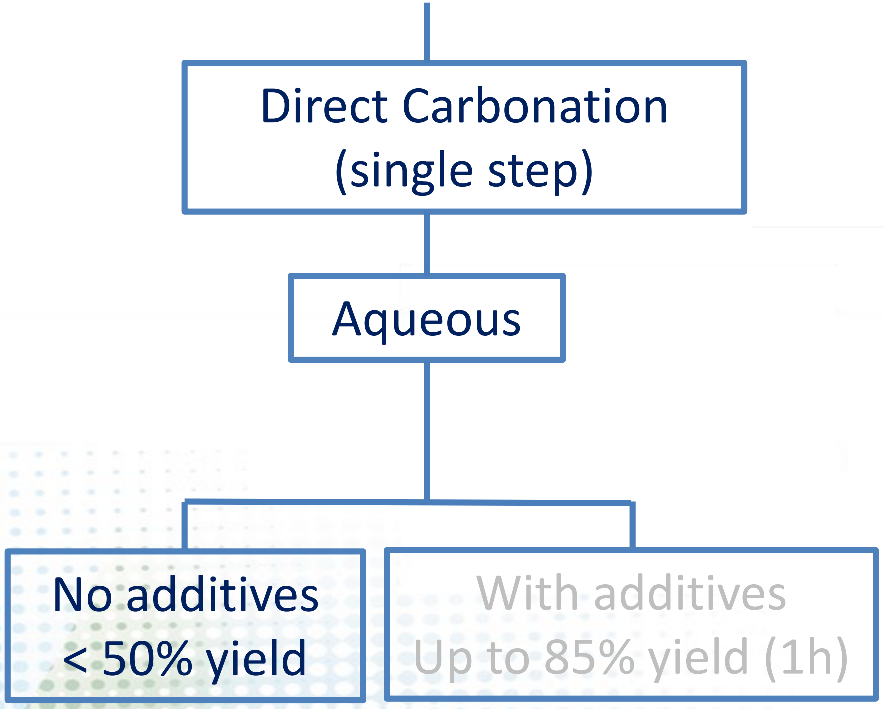
Si-catechol complex

(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



LGC

Studied MC pathways

Direct Carbonation (single step)

Aqueous

No additives
< 50% yield

> 50% yield?

With additives
Up to 85% yield (1h)

COUPLED ATTRITION-CARBONATION APPROACH

Continuous removal of ash layer

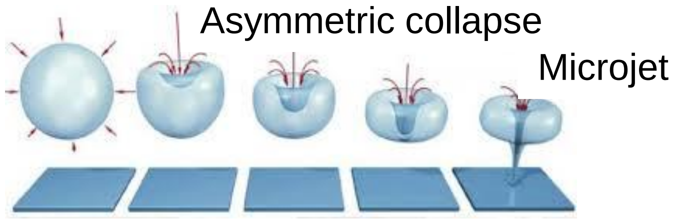
Physical exfoliation

Insensitive to ore type, no need for chemicals

State of the art

- ***High power ultrasound***

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



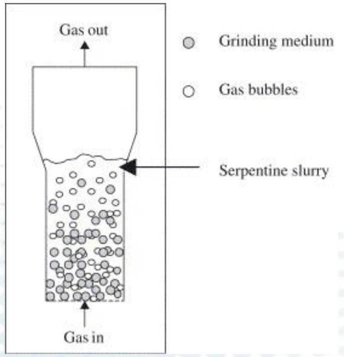
http://eswt.net/cavitation

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

- Mixed results

- ***Fluidized bed with grinding medium***

Park & Fan, 2004

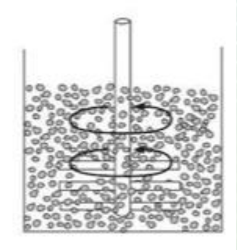


Might be difficult to control (density and/or size differences between reactive & inert particles), limited amount of grinding medium (20 wt.%)

- Some improvement of ore dissolution

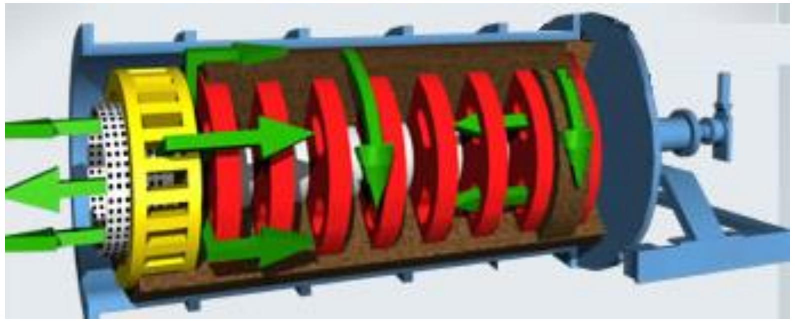
- ***Stirred tank with abrasive particles***

Chizmeshya et al., 2007



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

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 m^3

Issues:

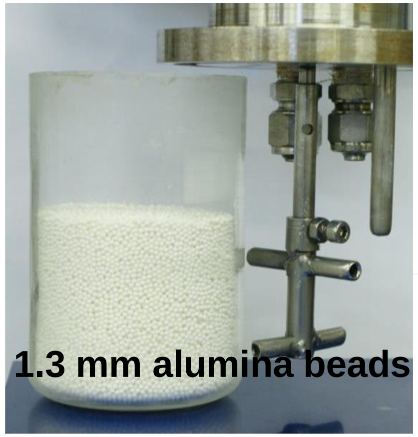
- (long-term) exfoliation efficiency?
  significant carbonation yield?
  within a reasonable solid residence time?
- passivation layer attrition *vs.* breakage of ore particles?

↓

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) – ω = 800 rpm



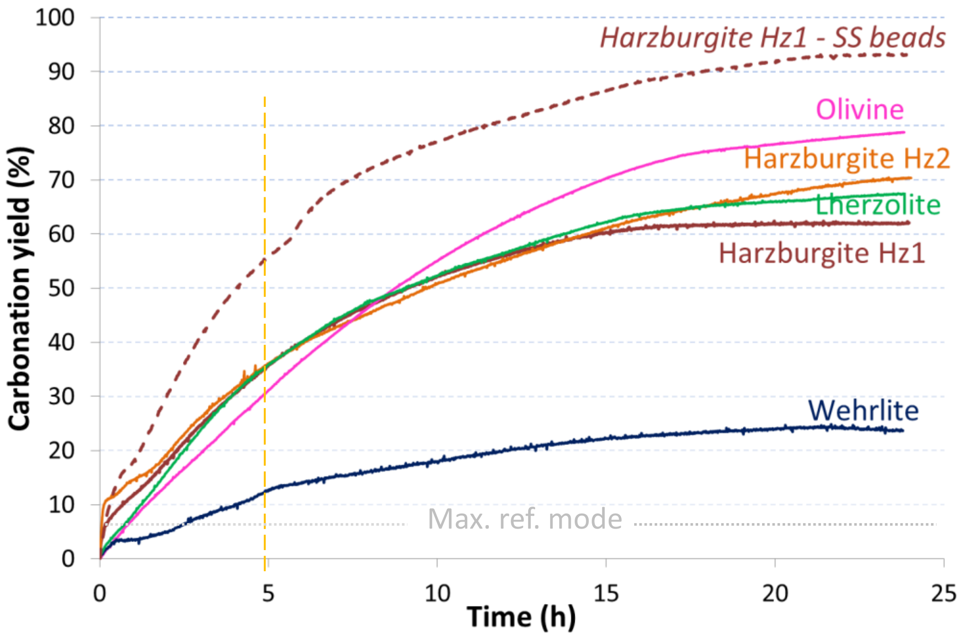
1.25-1.6 mm sand particles (99% SiO_2)

Carbonation tests

- **Reference case**
  Carbonation only
- **Two-step process**
  Attrition, followed by carbonation
- **Hybrid process**
  Coupled attrition-carbonation process

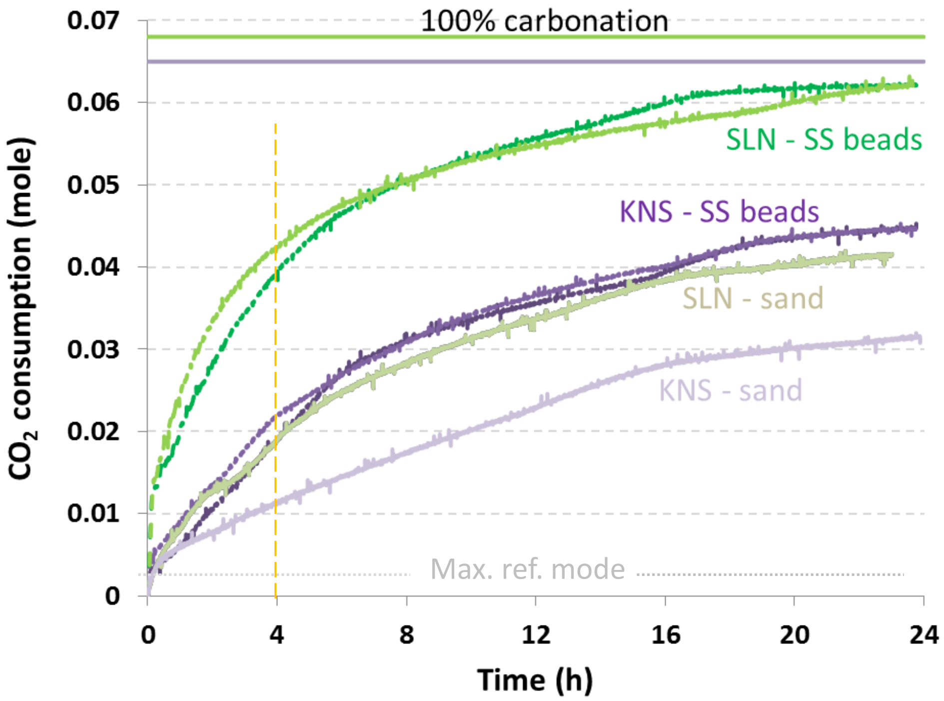
Proof of concept

Ores



Extent of carbonation for different ore types (180°C, 20 bar CO_2, ore conc.: 90 g/L, 1-2 mm Al_2O_3 —— or SS grinding media ---)

Slags

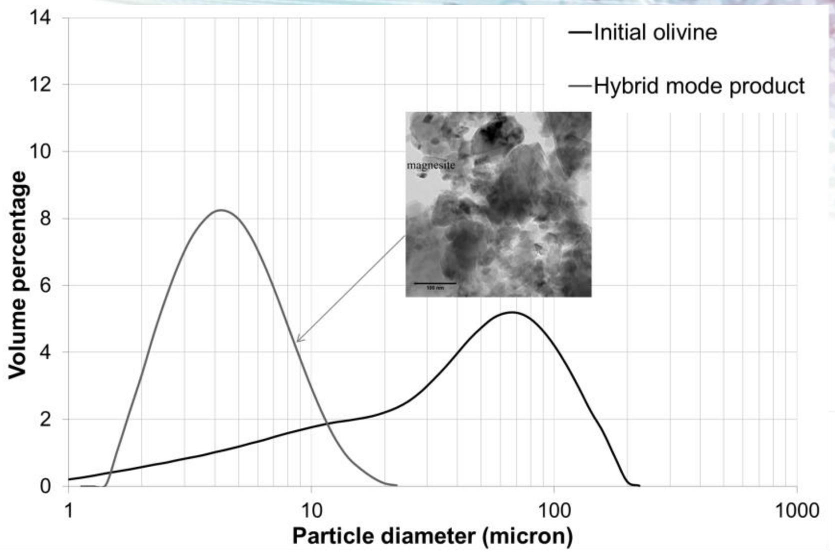


Extent of carbonation for different slag types (180°C, 20 bar CO_2, ore conc.: 90 g/L, 1-2 mm sand —— or SS grinding media ---)

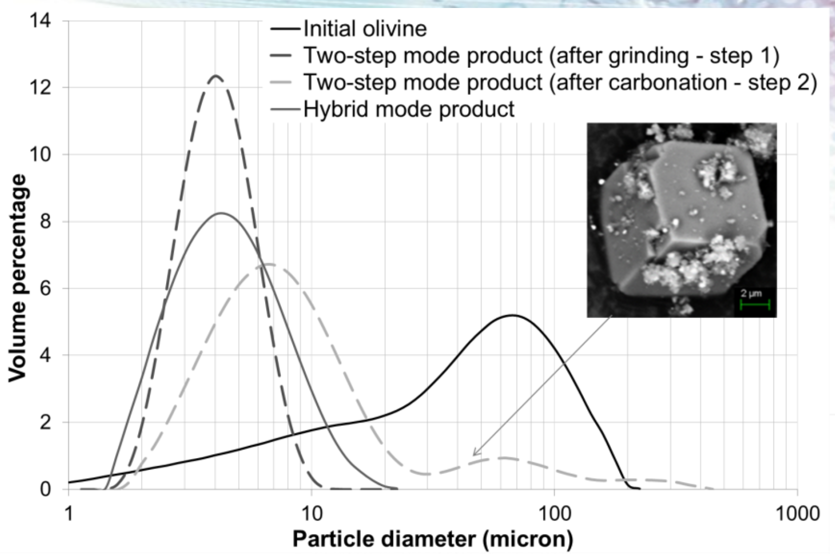
- Significant extent of carbonation (*vs.* < 8% in 24 h without attrition)
- Almost insensitive to ore type
- Noticeable influence of grinding medium

Proof of concept

Size effect only?

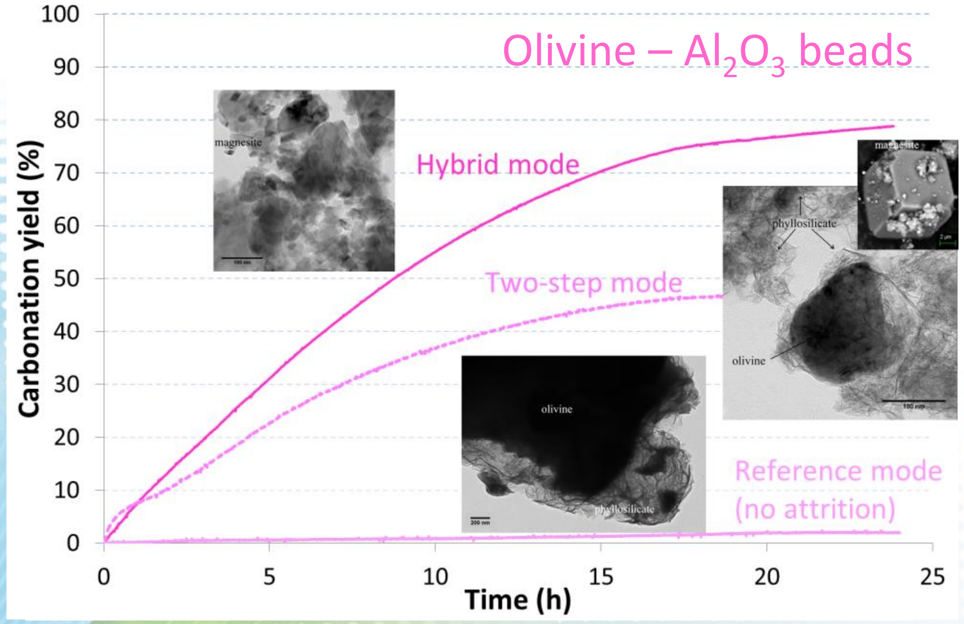


Proof of concept



Size effect only?

- Proof of synergy between attrition and leaching

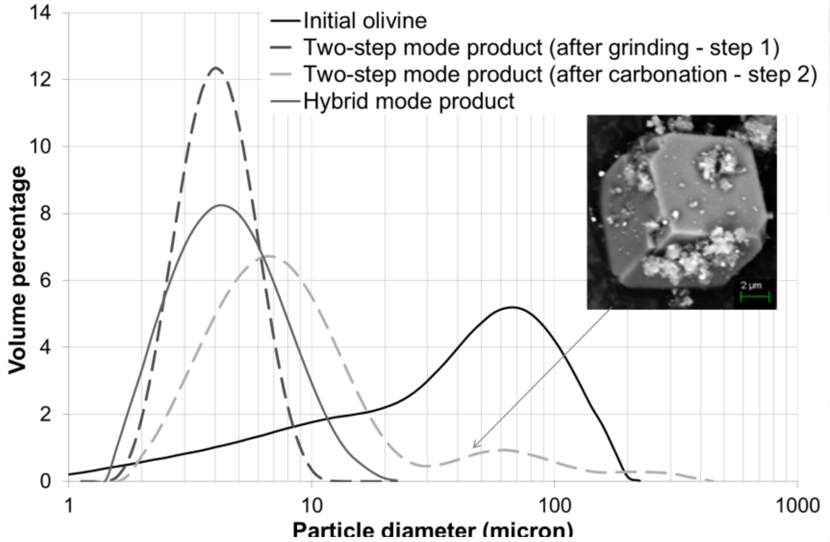


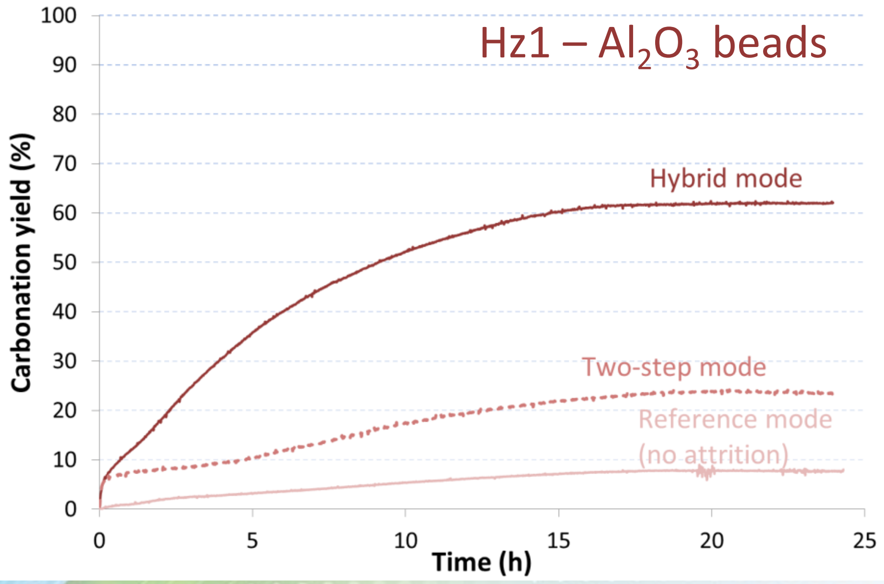
180°C, 20 bar CO_2, ore conc.: 90 g/L

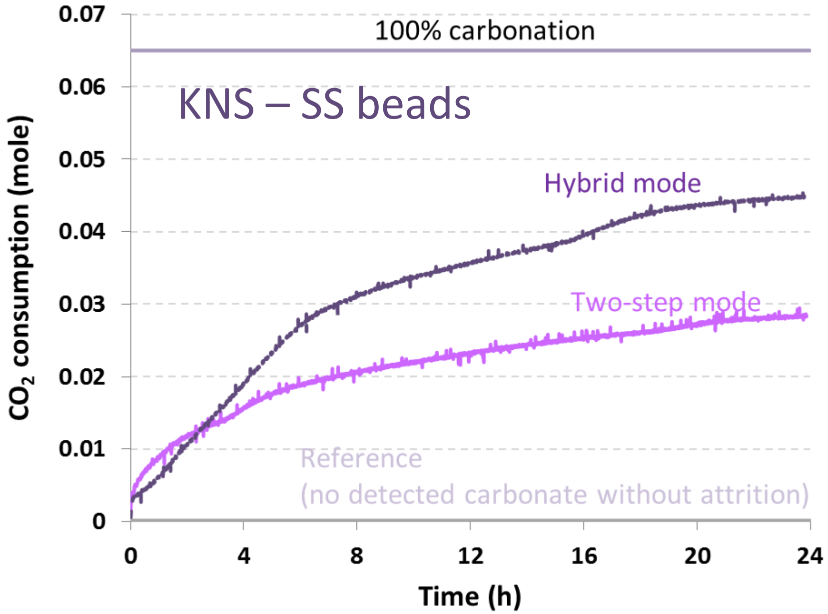
Proof of concept

Size effect only?

- Proof of synergy between attrition and leaching







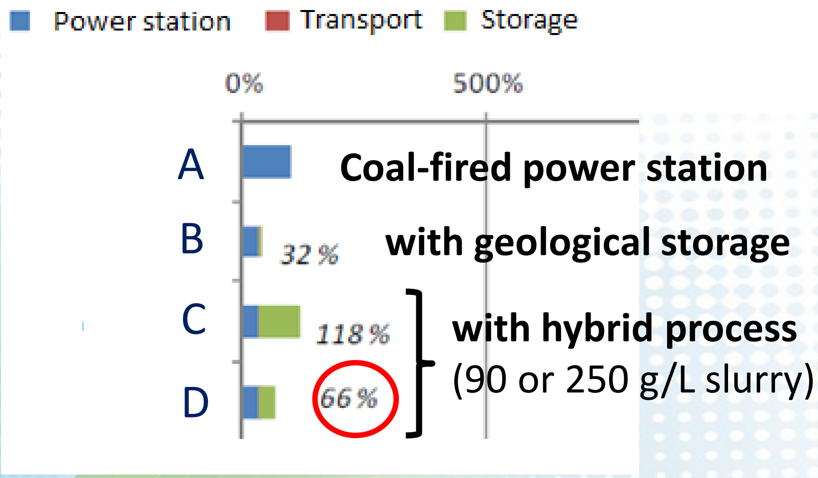
180°C, 20 bar CO_2, ore conc.: 90 g/L

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 CO_2 & 180°C
- CO_2 pipeline transport over a 300 km distance
- no recycling of process solution; no valorization of products

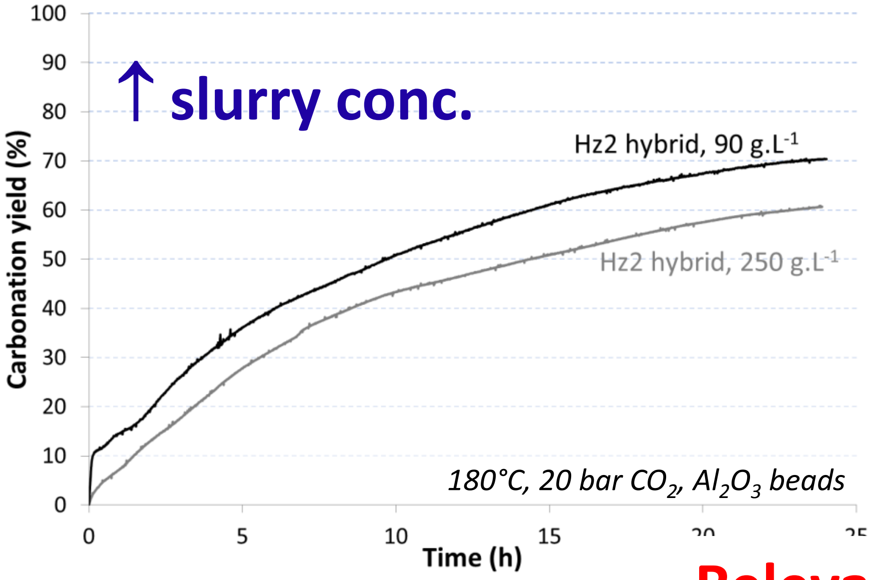
Impacts accounted for:
- CO_2 capture & compression
- crushing & milling of ore from 1 cm down to 100 µm
- mechanical energy expended for attrition
- reactants pre-heating & cooling (after heat integration)

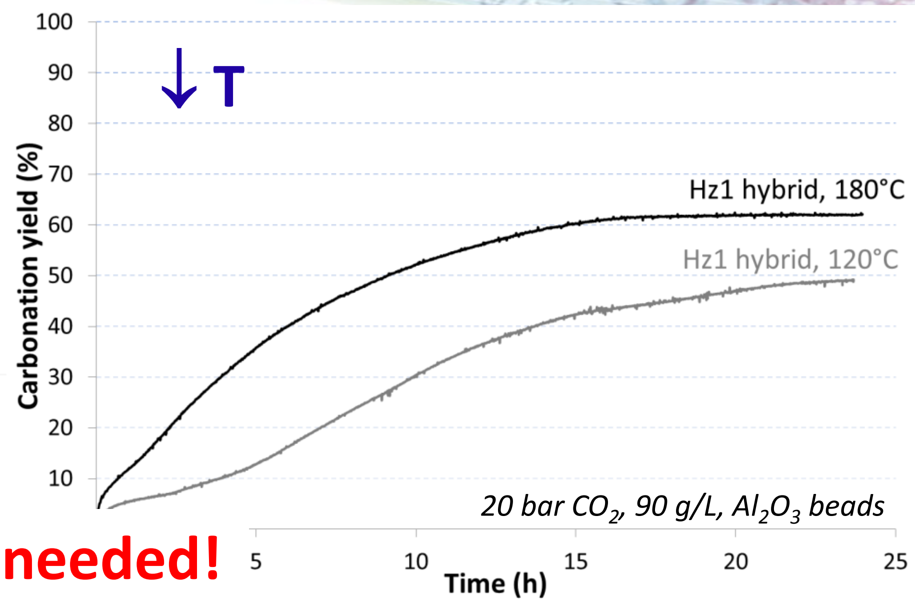


Net global warming potential (kg CO_2-eq)

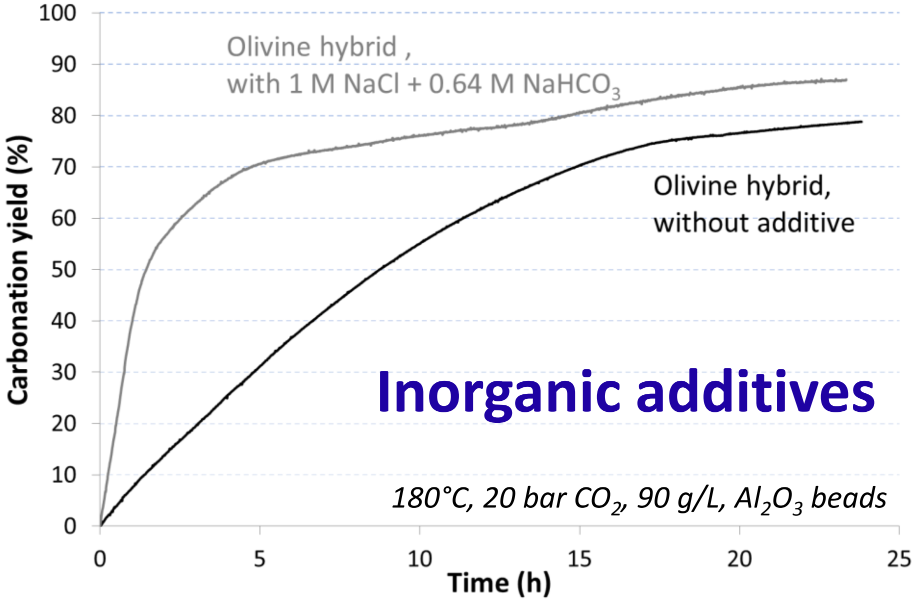
- ➢ Promising results regarding CO_2 avoided, without any process optimization
- ➢ Beneficiation of products & water recycling will also improve other LCA criteria (natural resource depletion +110% for case D)

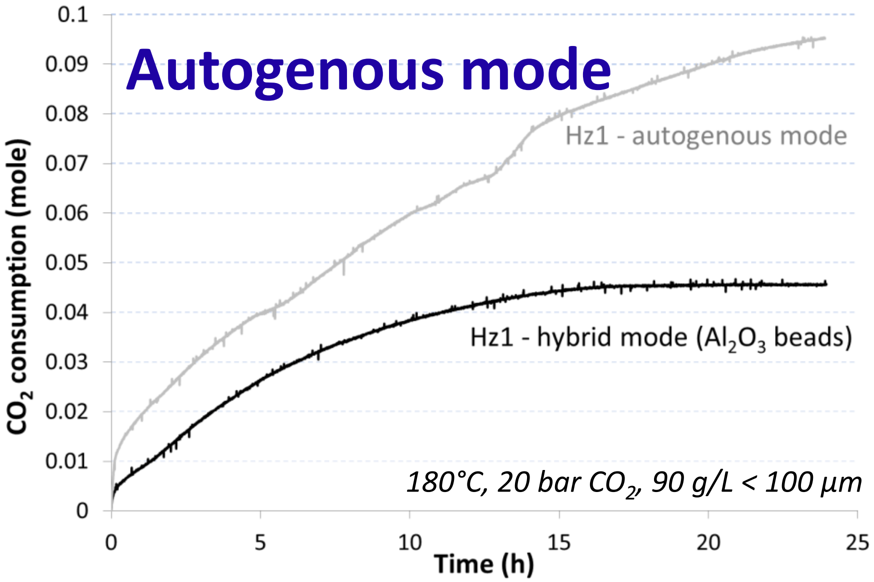
Possible ways of optimization





Relevant model is needed!





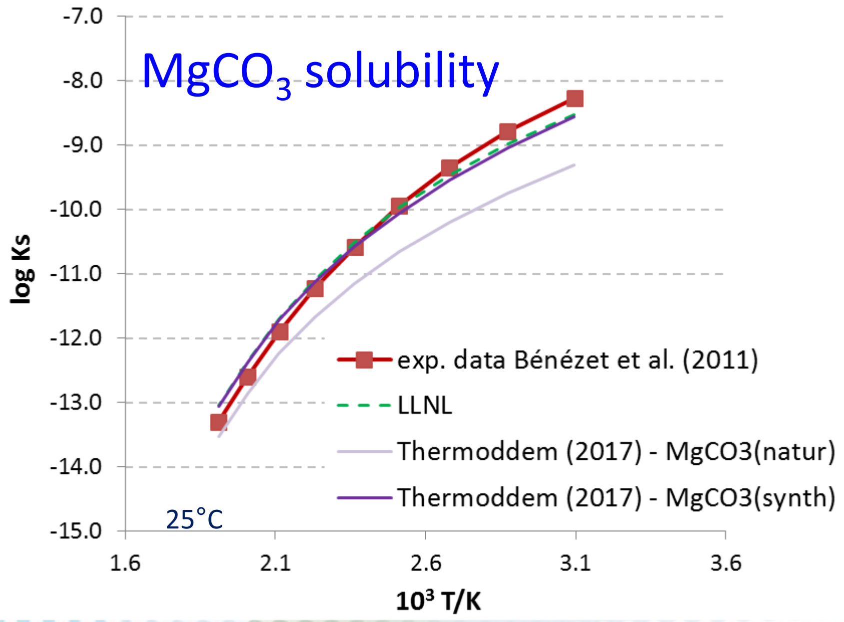
LGC

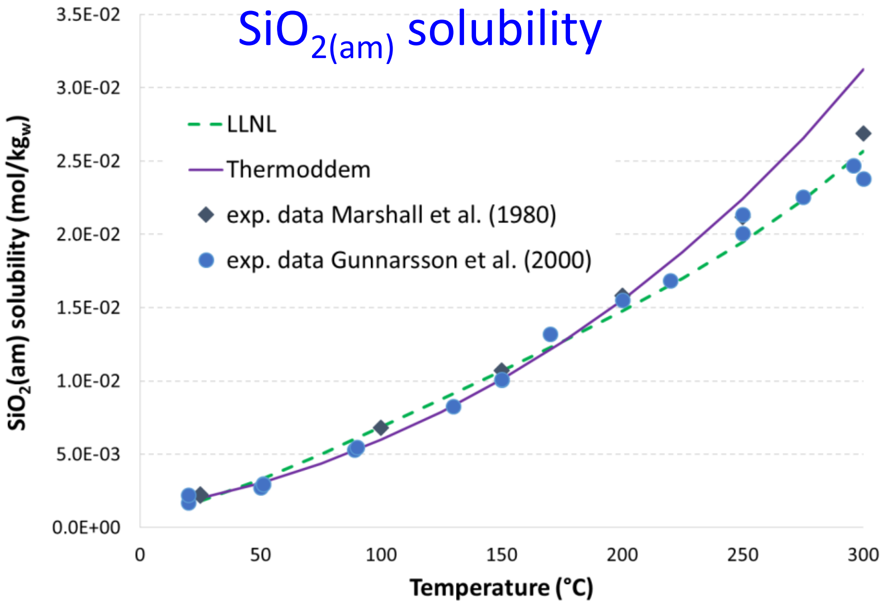
Geochemical modeling as a process design tool

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

Available databases: LLNL, Thermoddem

Selection based on existing exp. data for main system components





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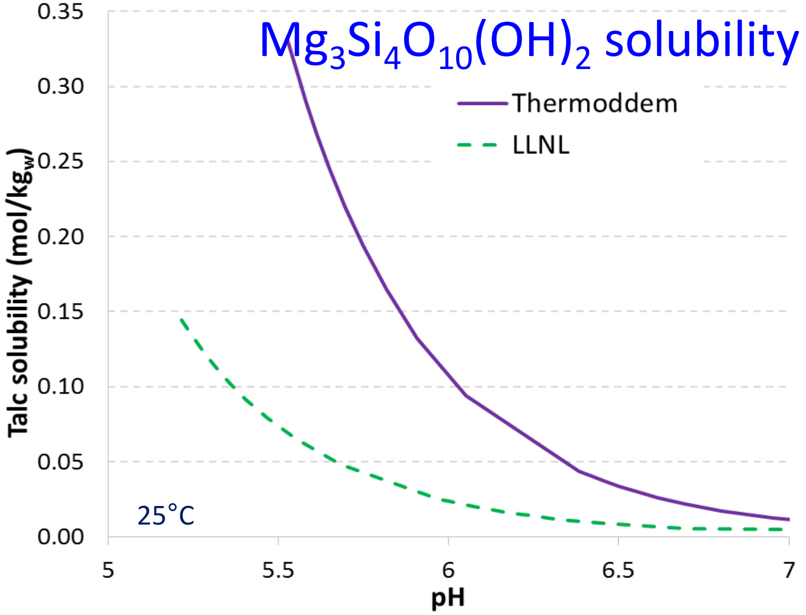
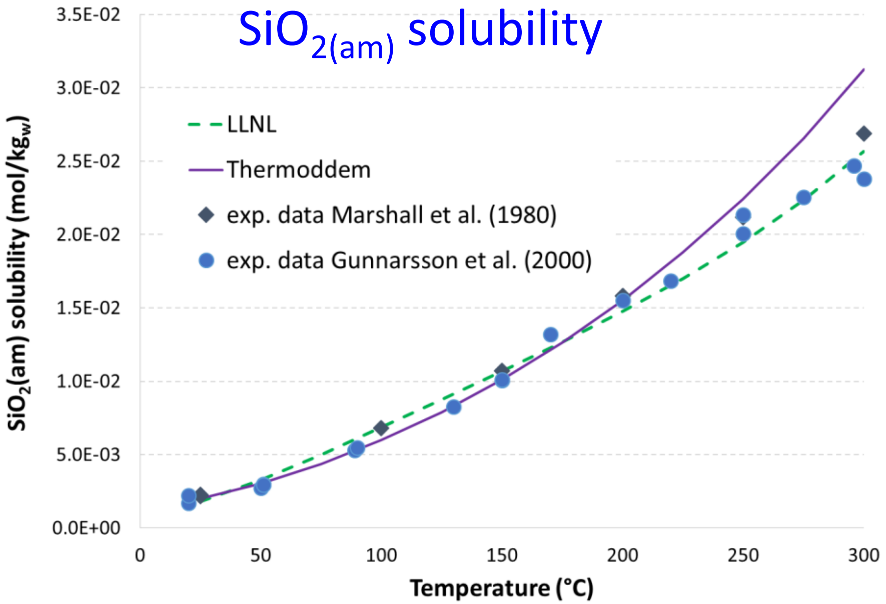




Discrepancies for talc, but no solubility data available (in similar conditions) → assessment on carbonation results

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

Gas: Peng-Robinson equation of state (non-ideal behavior of CO_2 - H_2O mixture at investigated P)

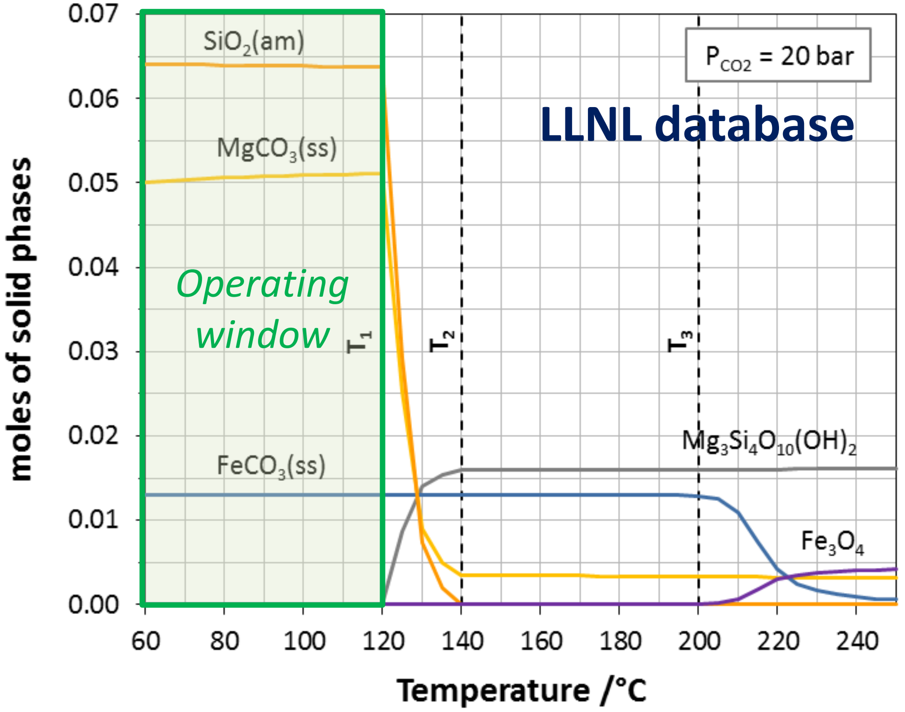
Solid: description of several **solid solutions** (e.g. $(Mg,Fe)CO_3$)

LGC

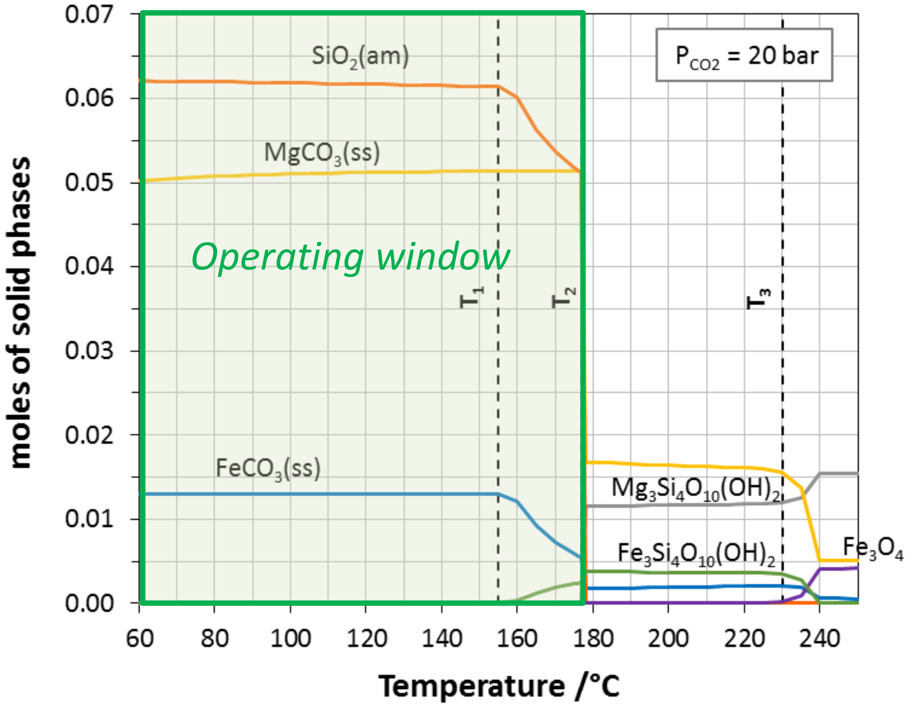
Case study 1: KNS / "inert" grinding medium

"KNS" (90 g/L) described as an assemblage of MgO, SiO_2 and FeO
All minerals including Mg, Si or Fe are allowed to precipitate, except quartz

Mineral speciation of KNS-H_2O-CO_2



Thermoddem 2017 database



- Threshold T for quantitative carbonation at 20 bar CO_2 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

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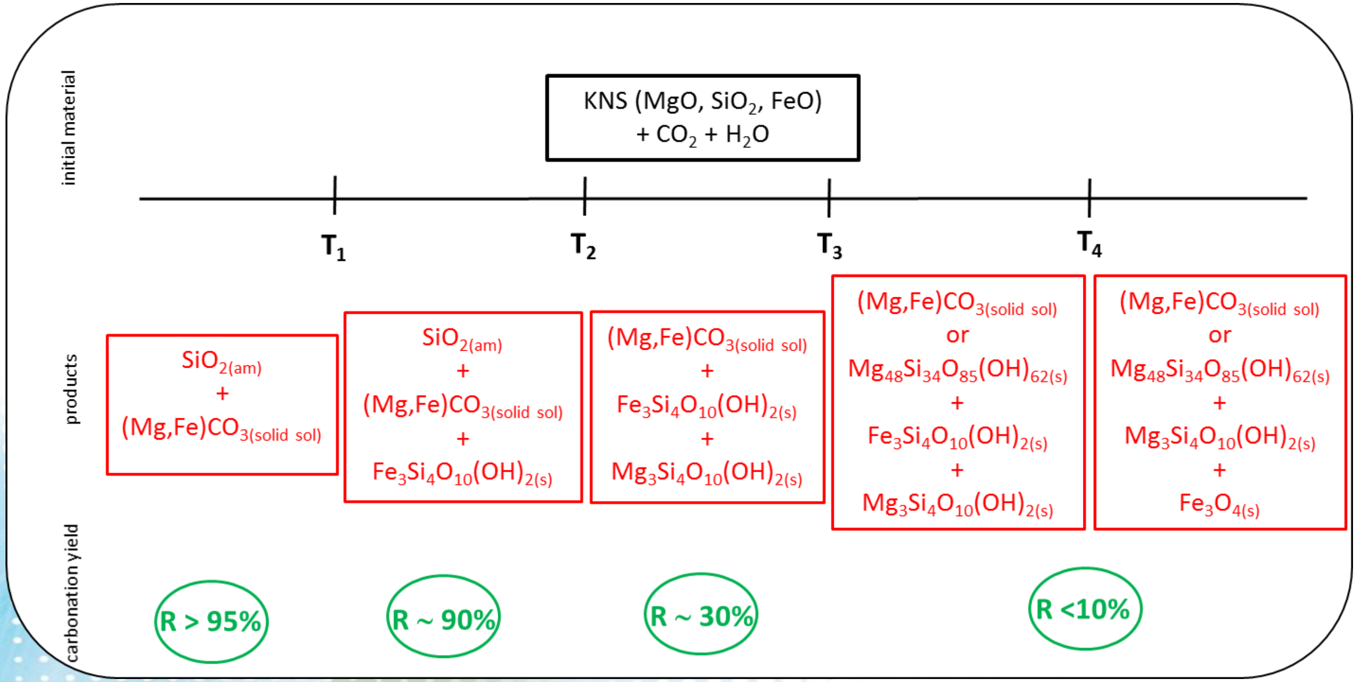
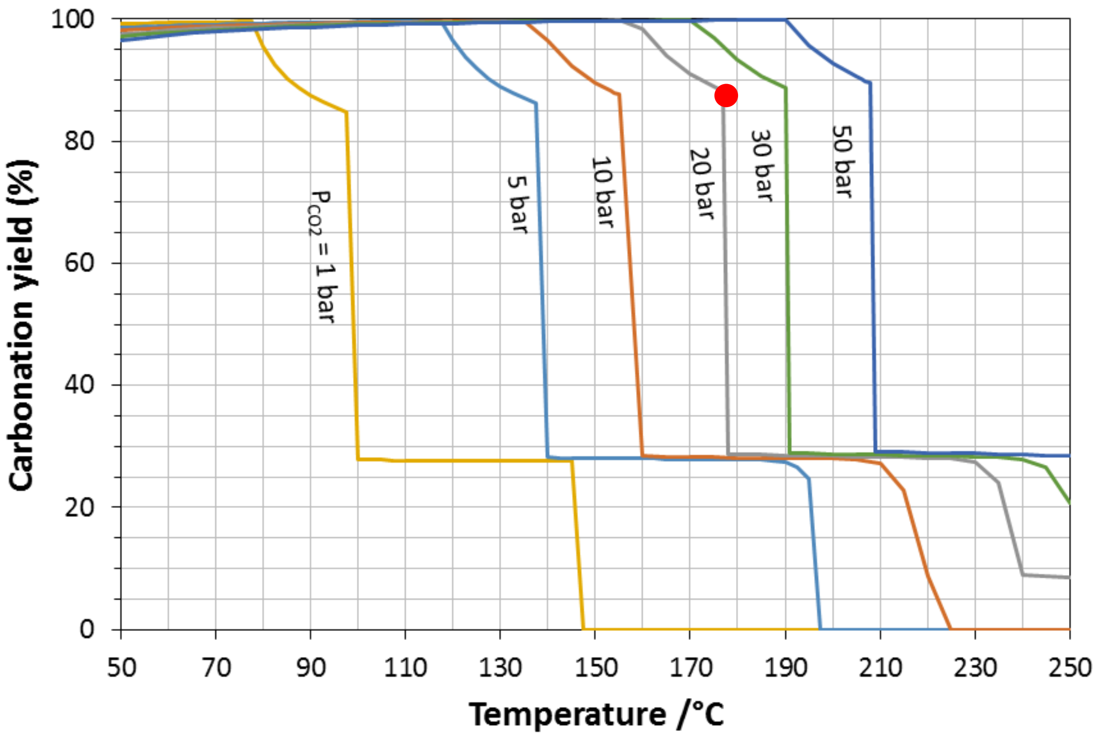
Thermoddem 2017





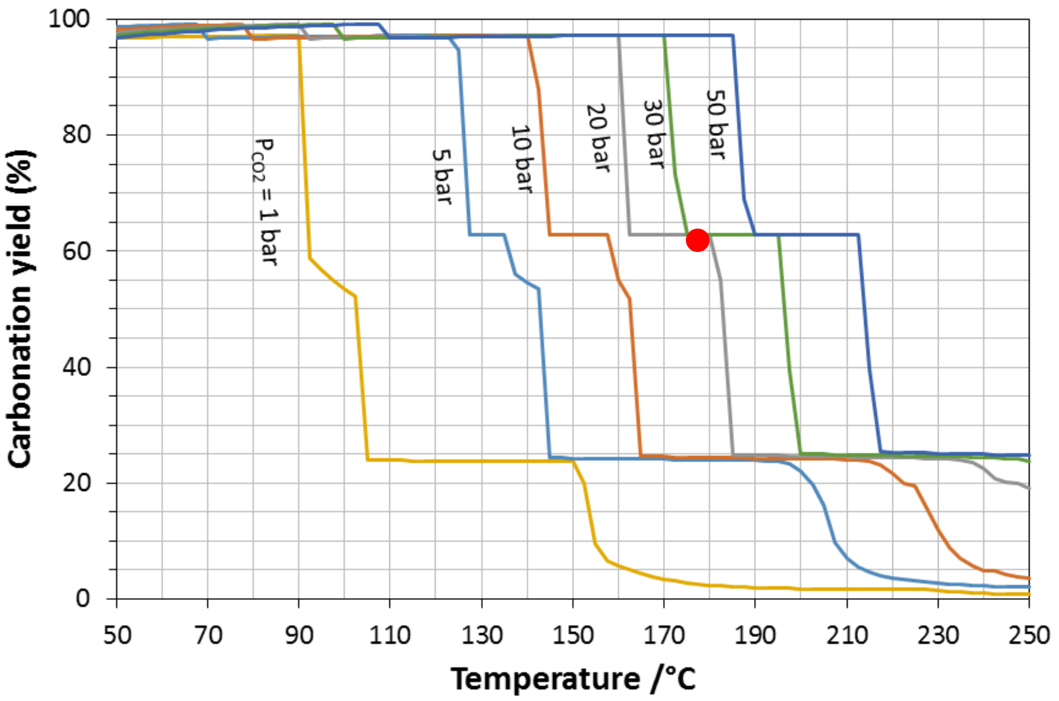
➢ Operating threshold temperature depends on P_{CO2}

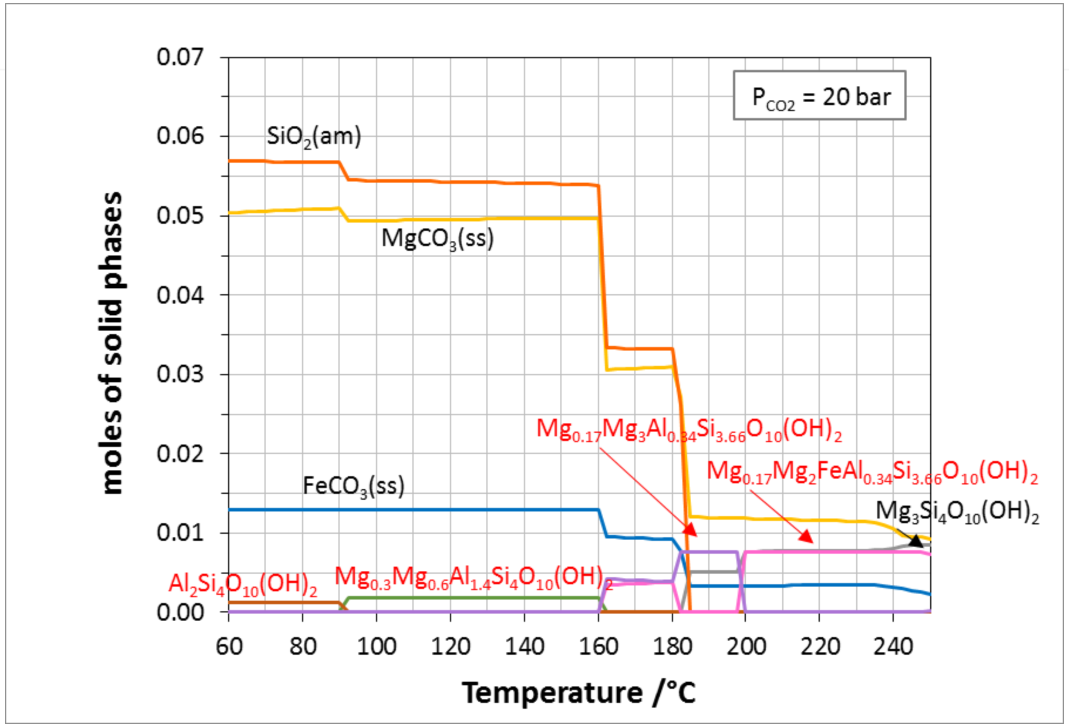
Case study 1: KNS / "inert" grinding medium

"KNS" (90 g/L) described as an assemblage of MgO, SiO_2, FeO, **CaO, Al_2O_3 and MnO**
All minerals including Mg, Si, Fe, **Ca, Al or Mn** allowed to precipitate (except quartz)

Mineral speciation of KNS-H_2O-CO_2

Thermoddem 2017



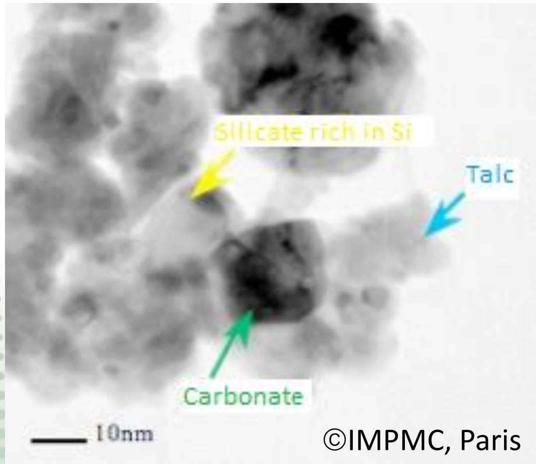


- The model predicts a noticeable effect of slag "impurities" (Al_2O_3 ~ 2%) due to the existence of various stable aluminosilicate phases

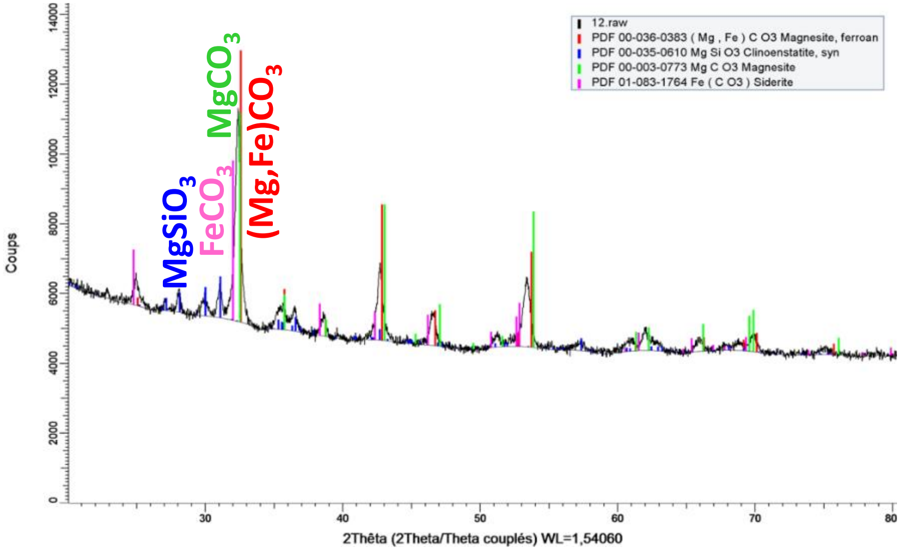
Case study 2: KNS / effect of grinding medium

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 &

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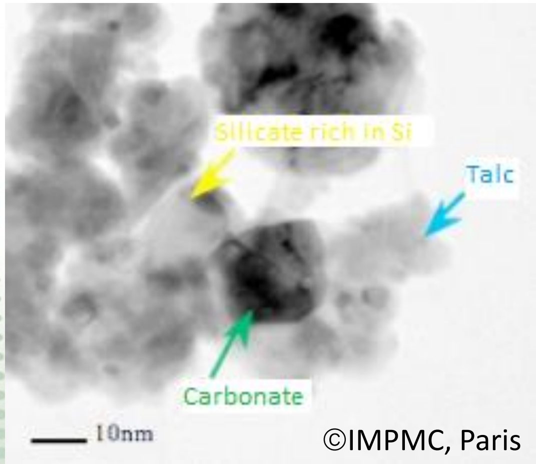
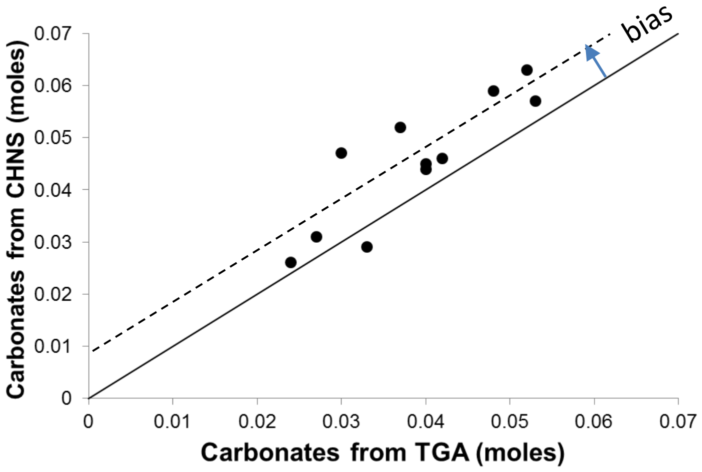


→ **Precipitation of various (amorphous) silicates**

– **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



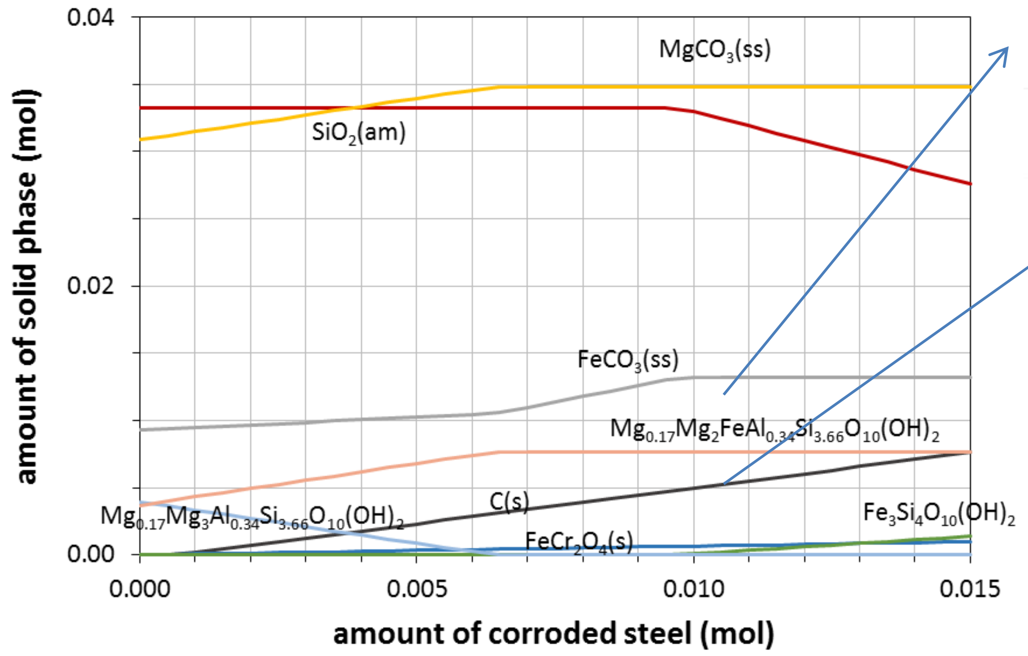
LGC

Case study 2: KNS / effect of grinding medium

"KNS" described as an assemblage of MgO, SiO_2, FeO, CaO, Al_2O_3 and MnO

Steel beads modeled as a $(Fe_{0.87}Cr_{0.13})$ solid solution

Mineral speciation of KNS-H_2O-CO_2

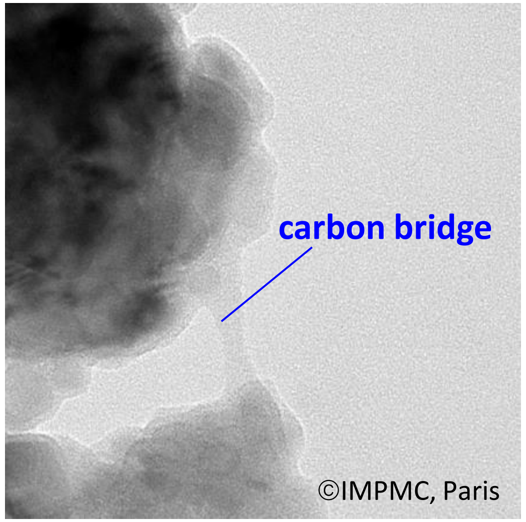


P_{CO2} = 20 bar, T = 175°C, slag conc. = 90 g/L

Fe extracted from beads as $FeCO_3$ & ferro-magnesium-aluminosilicate

Formation of solid carbon:

$$Fe_{(steel)} + 3/2\ CO_{2\ (aq)} = FeCO_{3\ (ss)} + 1/2\ C_{(s)}$$



➢ **Stainless steel beads are corroded during attrition-leaching under CO_2**

Case study 3: Batch simulation for olivine ore

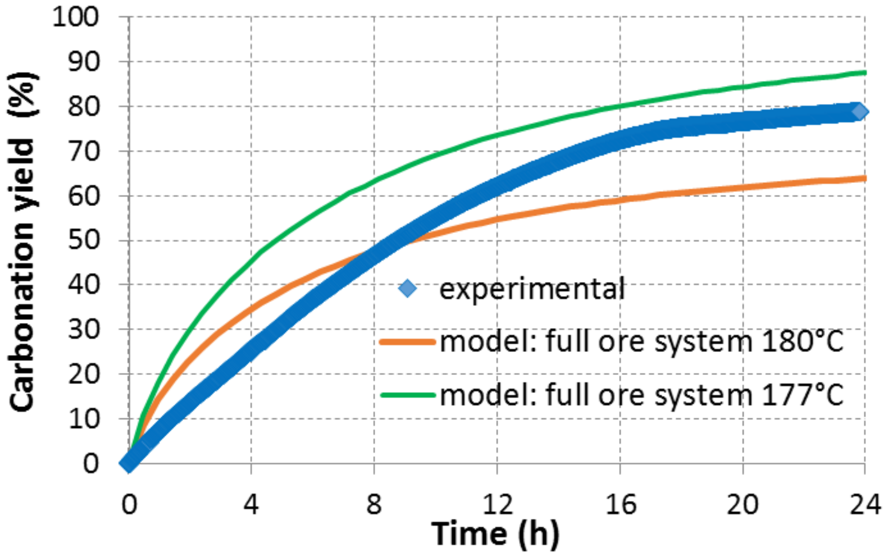
"Synthetic olivine" described as an assemblage of MgO, SiO_2, FeO, CaO, Al_2O_3 and MnO

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_{CO2} = 20 bar, T = 180°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**

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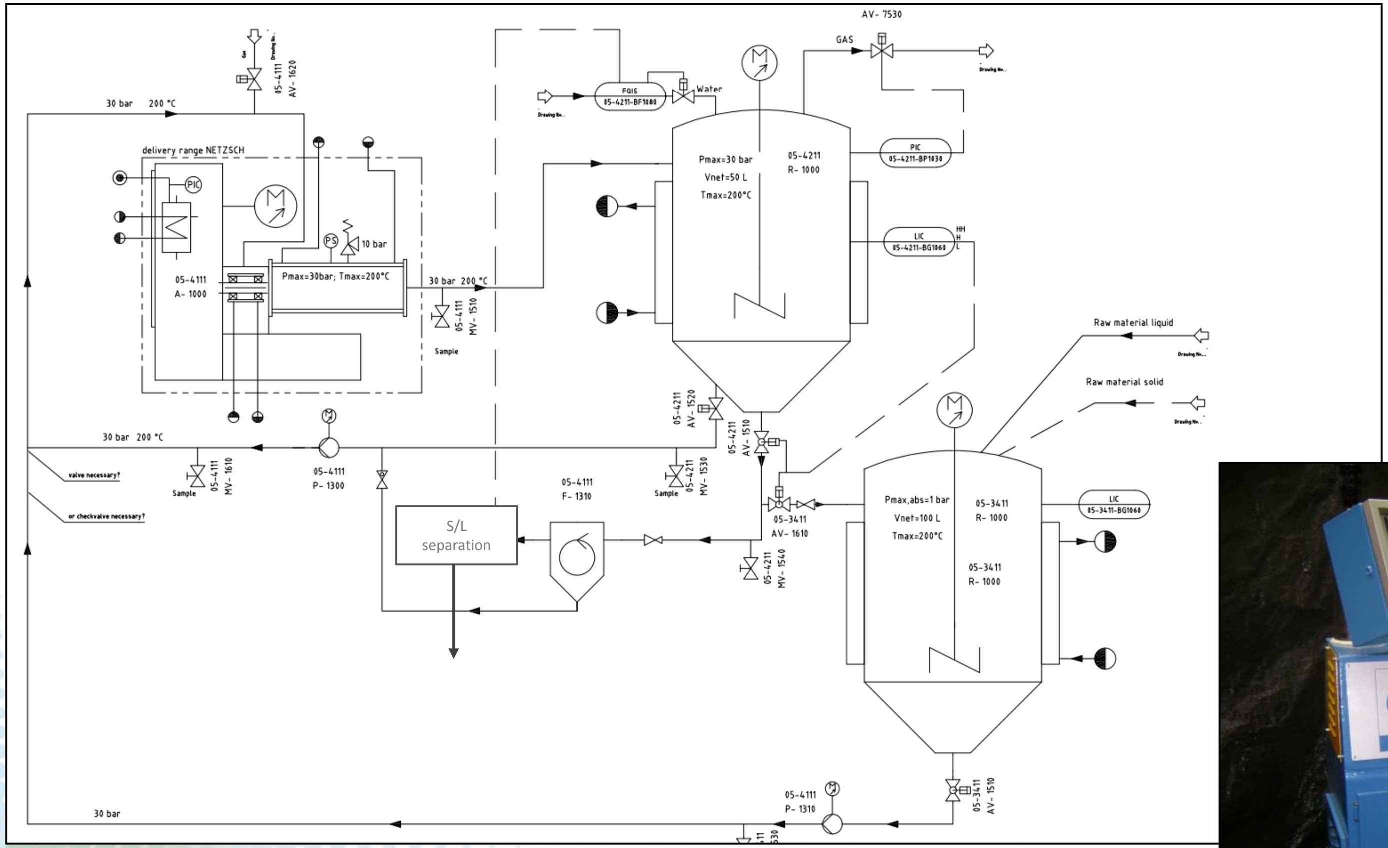
Continuous bench-scale process



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

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

cnrs

Université de Toulouse

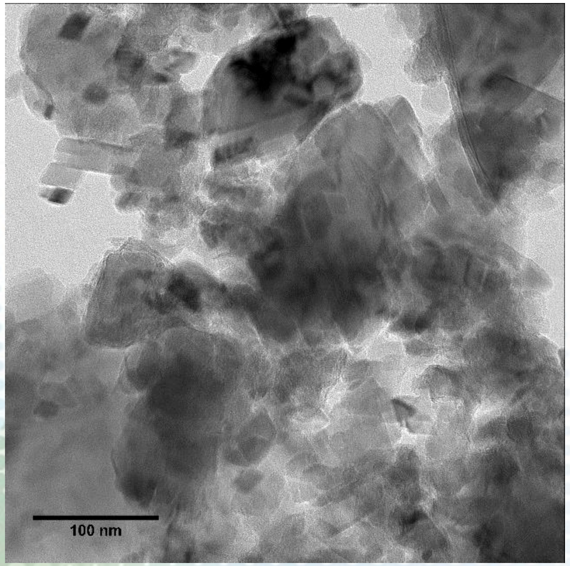
Utilization of MC products as construction or filling materials

- ➢ could in theory absorb Gt of CO_2 (approximately 33 billion tons of concrete produced / year)

✓ Potentially highly reactive additives

Hybrid process products:

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



almost "as it is" →

Inert filler or pozzolana (mainly ultra-fine silica fraction + $MgCO_3$)
CO_2 sequestered (& avoided)

after heating →

Hydraulic binder (mainly Mg rich fraction + SiO_2)
CO_2 avoided

Goal: valorization without solid separation & with minimum dewatering

- ✓ Virtuous CO_2 loop
- ✓ Reduction of natural resource depletion (no need for limestone)
- ✓ Reduction of heat demand ($T_{calcination}$ ↓)
- ✓ Local production of construction materials

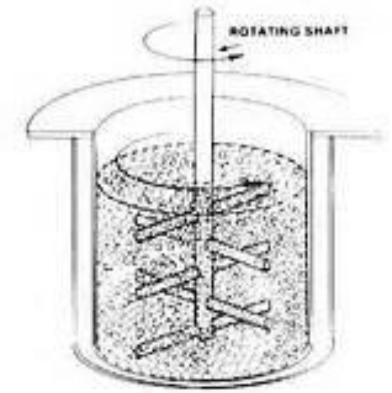
New concept: CCUS combined with Enhanced Metal Recovery

Innovative chemistry under attrition environment

Attrition-carbonation process

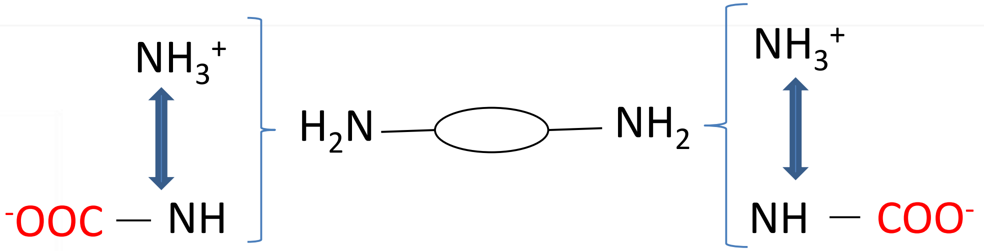
CO_2

(Ni) slags



\+

Polyamines



efficient CO_2 capture (dilute flue gases)

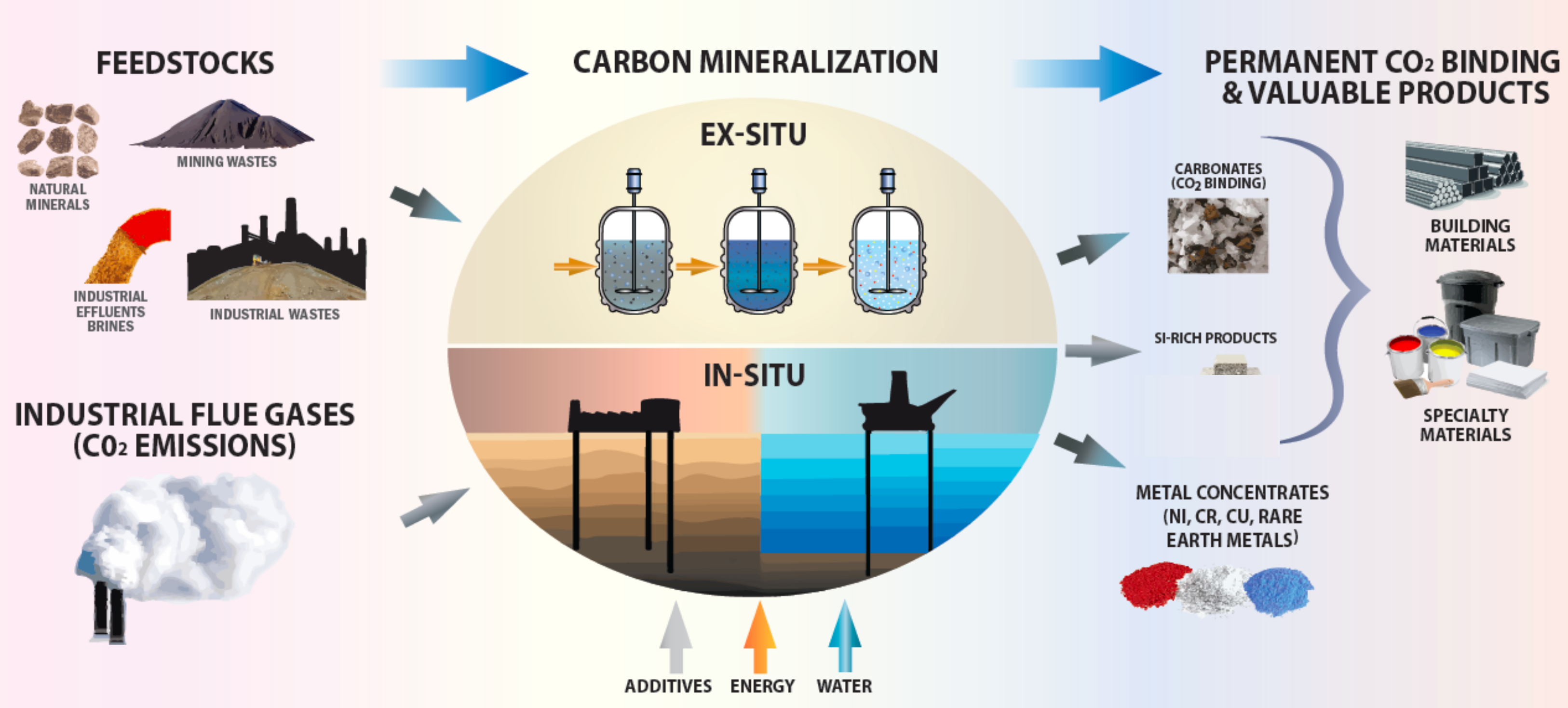
\+ catalysis of **CO_2 mineralization**

\+ potential modulation of silica precipitation

\+ selective **metal recovery**

Overall scheme for CO_2 mineralization

"Historically", CO_2 mineralization was compared to geological storage, in terms of storage cost and avoided CO_2: **Limited development ...**



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

In recent years, the mineralization of CO_2 systematically combines CO_2 storage and production of commercial goods, coupling environment and economy:

Booming development!

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J. Leclaire & J. Septavaux (**ICBMS Villeurbanne**)
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Thank you for your kind attention!

The actual team

CNRT NICKEL & son environnement

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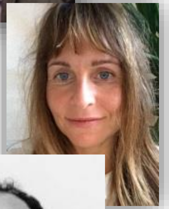
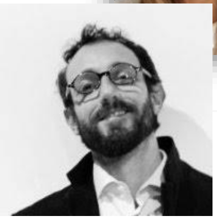
Dr. Carine Julcour



Dr. Laurent Cassayre



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