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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

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I. INTRODUCTION

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

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

Bench-scale continuous pilot
Valorisation route for MC products

CO₂ EMR
Collaborative work

CO₂ Enhanced Metal Recovery
Ex-situ Mineral Carbonation pathways

I. INTRODUCTION

Direct Carbonation (single step)
- Gas-solid
- Aqueous
- No additives < 50% yield
- With additives Up to 85% yield (1h)

Indirect Carbonation (2/multi-steps)
- Gas-solid
- Aqueous with additives 60-80% yield

Other approaches (brines, biomineralization ...)
- 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-CO₂/yr

High T, slow kinetics for natural ore
I. INTRODUCTION

Studied MC pathways

Direct Carbonation (single step)

Aqueous

No additives < 50% yield

With additives Up to 85% yield (1h)
I. INTRODUCTION

Surface leach layer & mechanisms

![Graph showing extraction yield over time with different layers: surface reaction controlled, diffusion controlled, passivated, ash layer, Phyllosilicate layer.]

- **Passivating** → No carbonate
  - Initial olivine
  - Phyllosilicate layer
  - FIB cross-sections of olivine particle after leaching (TEM) (Bodenan et al., 2014)

- **Diffusion controlling**
  - Carbonation yield < 10% (90 g/L, 95 h)
  - Initial olivine
  - Silica + iron oxide layer
  - 3 g/L (< 100µm), 20 bar CO₂, 120°C

**3 g/L (< 100µm), 20 bar CO₂, 120°C**

**90 g/L (< 100µm), 20 bar CO₂, 180°C**
Studied MC pathways

Direct Carbonation (single step)

Aqueous

No additives
< 50% yield

With additives
Up to 85% yield (1h)

EXPERIMENTAL METHODOLOGY
II. EXPERIMENTAL METHODOLOGY

Ores

Serpentinisation degree up to 90%

<table>
<thead>
<tr>
<th>Name</th>
<th>Origin</th>
<th>Dominating phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Harzburgite (Hz1)</td>
<td>New Caledonia</td>
<td>Serpentine (~90%) &gt;&gt; olivine &gt; orthopyroxene</td>
</tr>
<tr>
<td>Harzburgite (Hz2)</td>
<td>New Caledonia</td>
<td>Serpentine (~90%) &gt;&gt; olivine &gt; orthopyroxene</td>
</tr>
<tr>
<td>Wherlite (We)</td>
<td>New Caledonia</td>
<td>Serpentine (~50%) &gt; olivine &gt; clinopyroxene</td>
</tr>
<tr>
<td>Lherzolite (Lz)</td>
<td>France (Pyrenees)</td>
<td>Serpentine (~50%) &gt; olivine &gt; clinopyroxene</td>
</tr>
<tr>
<td>Olivine</td>
<td>Austria (Magnolithe)</td>
<td>Synthetic olivine (from high T dunite processing)</td>
</tr>
</tbody>
</table>

30.8 < MgO < 47.4%, 39.3 < SiO₂ < 46.3%, 7.3 < Fe₂O₃tot < 9.8%, 0.2 < CaO < 5.0%, 0.2 < Al₂O₃ < 4.0%
II. EXPERIMENTAL METHODOLOGY

Slags

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

<table>
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<tr>
<th>Name</th>
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</thead>
<tbody>
<tr>
<td>KNS</td>
<td>New Caledonia</td>
<td>Pyroxene: proto-enstatite, clinoenstatite, forsterite</td>
</tr>
<tr>
<td>SLN</td>
<td>New Caledonia</td>
<td>Vitreous fraction &gt;&gt; olivine</td>
</tr>
</tbody>
</table>

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

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

- **Mechanical sampling**

- **Initial particle size distribution**

  - **Ores**
    - 8-20% < 5 µm

  - **Ni slags**
    - 8-16% < 5 µm
II. EXPERIMENTAL METHODOLOGY

Carbonation set-up & procedure

• 300 mL autoclave reactor
• Controlled atmosphere (P_{CO2}) and T
• Gas auto-dispersing stirrer (800 rpm)
• Continuous recording of CO\textsubscript{2} consumption (24 h)

Solid 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

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

Laser diffraction analysis
Filtration (0.2 µm)

drying (70°C)
Studied MC pathway

- Direct Carbonation (single step)
  - Aqueous
    - With additives: Up to 85% yield (1h)
    - No additives: < 50% yield

CHELATING AGENT APPROACH
States of the art

- Effect of organic polyacids on dissolution rate

- Oxalate-enhanced dissolution rate

\[ r = \left( \frac{1 + \beta K x a_{ox}}{1 + K x a_{ox}} \right) r_{H^+} \]

\[ \approx 7 \] at 0.1 M oxalate (olivine, pH 5, 120°C)

Prigioibe & Mazzotti (2011)

Olsen & Rimstidt (2008)
Significantly improved extraction yield with oxalate at 3 g/L, but formation of solid by-product: **glushinskite** (MgC$_2$O$_4$.2H$_2$O)

Any compromise between glushinskite precipitation & Mg carbonation?
III. CHELATING AGENT APPROACH

**Oxalate-enhanced dissolution of olivine: effect of slurry concentration**

- **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?
Shrinking particle model

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

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

\[
r_{H^+} = k_0 \cdot \exp(-E_a/RT) \cdot a_{(H^+)}^n (1-10^{5l})
\]

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

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

III. CHELATING AGENT APPROACH

Oxalate-enhanced dissolution of olivine: kinetic modeling

surface reaction rate from Prigioobbe & Mazzotti (2011)
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

![Graph showing extraction yield over time](image)

**Simulation with CHESS code (van der Lee, 2007)**
- 120°C, 20 bar CO₂,
- 3 g/L olivine < 100 µm
- after estimation of precipitation rate constants for silica & talc

**Bonfils et al. (2012)**
- Good agreement with experimental data at 3 g/L
  → chemical controlled reaction
Oxalate-enhanced dissolution of olivine: geochemical modeling (with CHESS)

**Issues:**
- Mg-oxalate species missing in used thermodynamic database (CTDP)
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- → dedicated precipitation experiments at 120°C & database updating

- Good agreement with experimental data at 3 g/L
  → chemical controlled reaction
Organic polyacid salts (oxalate, citrate, EDTA): too strong Mg binders for MC at moderate $P_{\text{CO}_2}$

Alternative option: silica(te) layer modulation / impeding by ligands

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

Oxalate

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

Catechol

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

Si-catechol complex

(Barnum, 1970; Russo-Mascioli, 2001)
Studied MC pathways

Direct Carbonation (single step)

Aqueous

No additives
< 50% yield

With additives
Up to 85% yield (1h)
Studied MC pathways

Direct Carbonation (single step)

Aqueous

COUPLED ATTRITION-CARBONATION APPROACH

No additives
< 50% yield

> 50% yield?

With additives
Up to 85% yield (1h)

Continuous removal of ash layer

Physical exfoliation

Insensitive to ore type, no need for chemicals
IV. COUPLED ATTRITION-CARBONATION APPROACH

State of the art

- **High power ultrasound**
  
  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

- **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.%)
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) – \( \omega = 800 \text{ rpm} \)

1.3 mm alumina beads

1.6 mm stainless steel (SS) beads

1.25-1.6 mm sand particles (99% SiO\(_2\))

**IV. COUPLED ATTRITION-CARBONATION APPROACH**

**Carbonation tests**

- **Reference case**
  - Carbonation only

- **Two-step process**
  - Attrition, followed by carbonation

- **Hybrid process**
  - Coupled attrition-carbonation process
IV. COUPLED ATTRITION-CARBONATION APPROACH

Proof of concept

**Ores**

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

**Slags**

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

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*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 —)*

*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 —)*
IV. COUPLED ATTRITION-CARBONATION APPROACH

Proof of concept

Size effect only?
Size effect only?

- Proof of synergy between attrition and leaching

IV. COUPLED ATTRITION-CARBONATION APPROACH

Proof of concept

180°C, 20 bar CO$_2$, ore conc.: 90 g/L
Size effect only?

- Proof of synergy between attrition and leaching

**IV. COUPLED ATTRITION-CARBONATION APPROACH**

### Proof of concept

**Hz1 – Al$_2$O$_3$ beads**

**KNS – SS beads**

- **Hybrid mode**
- **Two-step mode**
- **Reference mode** (no attrition)

180°C, 20 bar CO$_2$, ore conc.: 90 g/L
**Functional unit:** 1 MWhe with a coal-fired power station

**Main hypotheses:**
- Yield of ~ 80% in 24 h at 20 bar CO<sub>2</sub> & 180°C
- CO<sub>2</sub> pipeline transport over a 300 km distance
- No recycling of process solution; no valorization of products

**Impacts accounted for:**
- CO<sub>2</sub> 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)

- Promising results regarding CO<sub>2</sub> 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

IV. COUPLED ATTRITION-CARBONATION APPROACH

Inorganic additives

Autogenous mode

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)

Available databases: LLNL, Thermoddem

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

- 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

“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

Operating threshold temperature depends on $P_{\text{CO}_2}$
Case study 1: KNS / “inert” grinding medium

“KNS” (90 g/L) described as an assemblage of MgO, SiO$_2$, FeO, CaO, Al$_2$O$_3$ and MnO
All minerals including Mg, Si, Fe, Ca, Al or Mn allowed to precipitate (except quartz)

Mineral speciation of KNS-H$_2$O-CO$_2$

- The model predicts a noticeable effect of slag “impurities” (Al$_2$O$_3$ ~ 2%) due to the existence of various stable aluminosilicate phases

Thermoddem 2017
IV. COUPLED ATTRITION–CARBONATION APPROACH

Case study 2: KNS / effect of grinding medium

Experimental data

- Carbonation yield $\sim 50\%$ 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 &
IV. COUPLED ATTRITION–CARBONATION APPROACH

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 MgCO₃ pole)
- TEM/EDX

→ 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
Stainless steel beads are corroded during attrition-leaching under CO₂

IV. COUPLED ATTRITION-CARBONATION APPROACH

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 (Fe₀.₈₇Cr₀.₁₃) solid solution

Mineral speciation of KNS-H₂O-CO₂

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

Formation of solid carbon:

\[
\text{Fe (steel) + } \frac{3}{2} \text{CO}_2 (\text{aq}) = \text{FeCO}_3 (\text{ss}) + \frac{1}{2} \text{C (s)}
\]

\[P_{\text{CO}_2} = 20 \text{ bar}, T = 175°C, \text{ slag conc.} = 90 \text{ g/L}\]
“Synthetic olivine” described as an assemblage of MgO, SiO$_2$, FeO, CaO, Al$_2$O$_3$ 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)

Case study 3: Batch simulation for olivine ore

Time-evolution of carbonation yield

“Inert” grinding medium

Effect of alumina grinding beads

- Very slow dissolution kinetics
  → Negligible effect on system speciation

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

- 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
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

Continuous bench-scale process
Utilization of MC products as construction or filling materials

- Hybrid process products: agglomerates of nano-sized particles of carbonates, silica & silicates
  - 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

- Potentially highly reactive additives

Could in theory absorb Gt of CO₂ (approximately 33 billion tons of concrete produced / year)
New concept: CCUS combined with Enhanced Metal Recovery

Innovative chemistry under attrition environment

V. CONCLUSIONS: ONGOING & FUTURE WORK

Efficient CO$_2$ capture (dilute flue gases)

+ catalysis of CO$_2$ mineralization

+ potential modulation of silica precipitation

+ selective metal recovery
"Historically", CO\textsubscript{2} mineralization was compared to geological storage, in terms of storage cost and avoided CO\textsubscript{2}:

Limited development ...

Overall scheme for CO\textsubscript{2} mineralization

"Historically", CO\textsubscript{2} mineralization was compared to geological storage, in terms of storage cost and avoided CO\textsubscript{2}:

Limited development ...

In recent years, the mineralization of CO\textsubscript{2} systematically combines CO\textsubscript{2} storage and production of commercial goods, coupling environment and economy:

Booming development!

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