Baltic Carbon Forum 2023

MAGNEX and PILCCU in Finland: deployment of CO_2 mineralisation in circular economies

Ron Zevenhoven prof.

ÅA Chem. & Proc. Eng.

12-13.10.2023 Riga, Latvia

Åbo Akademi University

Two projects:
the academic researchers and PIs.

- Business Finland ”leading companies” PILCCU 2022-2024
  - ÅA: **Ron Zevenhoven**, Nico Häggqvist, Evelina Koivisto
  - Univ. of Oulu: **Päivö Kinnunen**, Hellen Silva Santos, Hoang Nguyen, Kanwal Shahid, Harri Haapasalo, Jukka Majava, Sudeep Parajuli
  - Oulu Mining School: Sanna Luukkanen, Sampo Haapasaari, Markku Seitsaari
  - Geological Survey of Finland (GTK): **Heikki Pirinen**, Tegist Chernet, Neea Heino, Pasi Heikkilä, Tapio Halkoaho, Hanna Kaasalainen, ….
  - Lappeenranta-Lahti Univ. of Technology: **Jarkko Levänen**, Katariina Buure, Laura Kainiemi

- Academy of Finland project MAGNEX 2022-2025
  - Univ. of Oulu: **Päivö Kinnunen**, Hellen Silva Santos
  - ÅA: **Ron Zevenhoven**, Jens Back, Evelina Koivisto
  - Tampere Univ.: **Erkki Levänen**, Arnold Ismailov

PILCCU 2022-2024

Mining industry

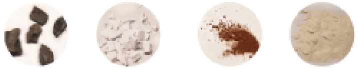
Magnesium silicate mining wastes

+

CO_2 from human activities

CO_2 mineral carbonation process routes

Magnesium carbonate hydrates + silica + metals



Piloting carbon capture and utilization (CCU)

via

CO_2 mineral sequestration of potentially millions of tons of CO_2 per year

using

magnesium-rich mining tailings and waste rock from Finland

producing

magnesium carbonate, silica & metals with market value

with

acceptance from society.

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University of Oulu

GTK

LUT University

NESTE

Metso:Outotec

BERNER

BUSINESS FINLAND

ELEMENTIS

SAINT-GOBAIN

outokumpu

FINNSEMENTTI A CRH COMPANY

Renotech Oy

Objectives

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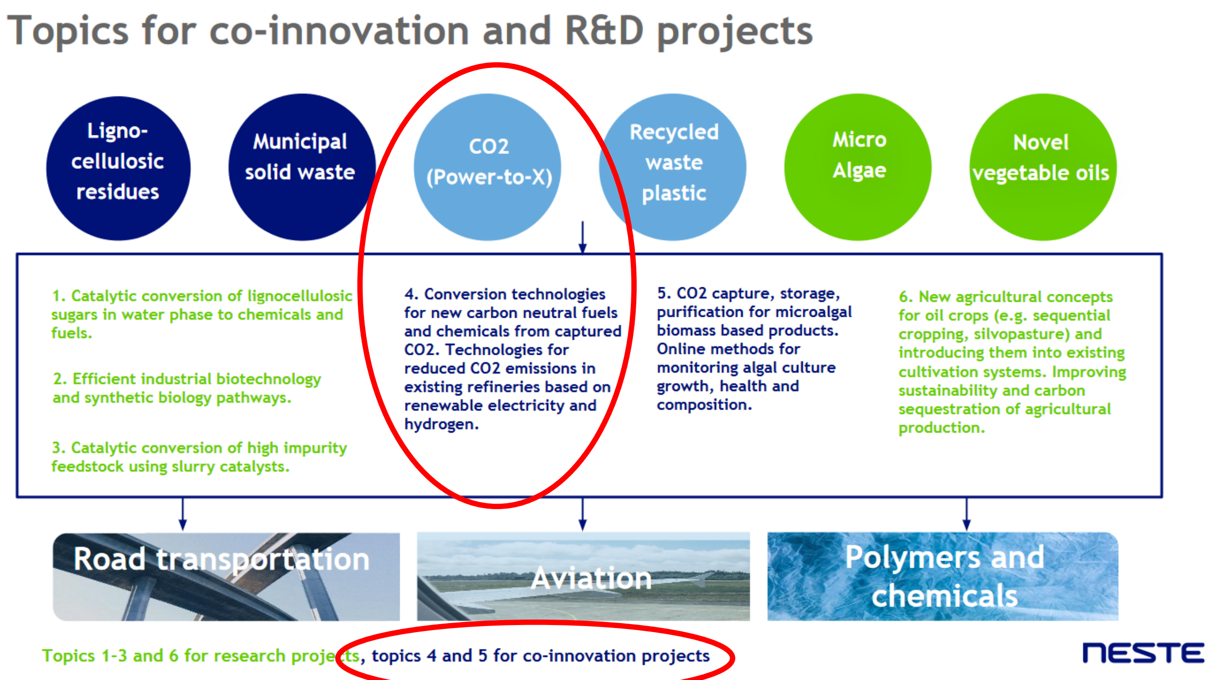
- See https://www.businessfinland.fi/4a694f/globalassets/finnish-customers/01-funding/06-ecosystems/neste_veturi_tiekartta.pdf



Objectives, needs & team input

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- Mineralisation of large amounts (>> 0.1 Mt/yr) of CO_2 using the ÅA routes for CO_2 mineral sequestration using (preferably) serpentinite
- 2-year feasibility + rough design of Pilot plant (for Neste Porvoo & ….) (→ 2½ years)
- 2-year more detailed design (pre-FEED) and critical components testing

- Skills and scientific / industry sector input needed:
  - The ÅA routes: select from 5 routes based on CO_2 emitting process
  - *Suitable rock resources inside Finland (update and more detail)*
  - *Supply chain of rock and chemicals and industrial scale rock processing*
  - *Use of carbonate products in green cement or for thermal energy storage (TES)*
  - *Analysis of social acceptance, policy studies and life-cycle assessment*
  - *The large-scale engineering (mainly Phase II)*
  - *Other large CO_2 emission point sources in Finland and abroad (NL, SG)*
  - *International academic cooperation (DE, UK, ZA, LV)*
  - *Industrial ecosystem development and productisation*

5 ÅA-routes for serpentinite carbonation

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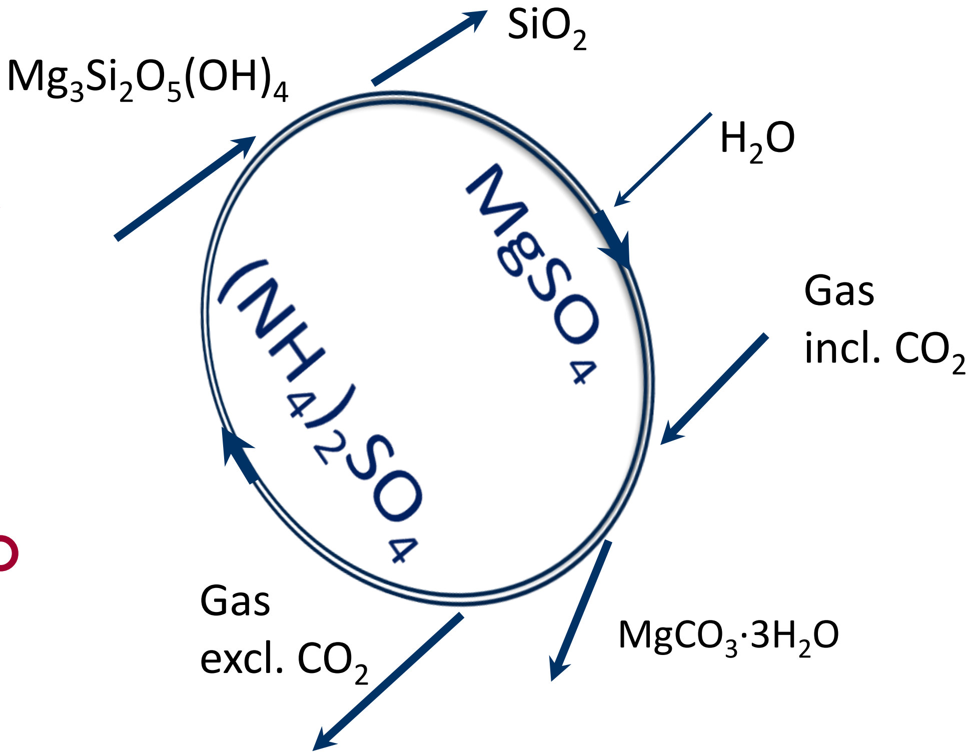
$Mg_3Si_2O_5(OH)_4$ + $3(NH_4)_2SO_4$
(optional: + heat 440°C) ←→
$3MgSO_4 + 2SiO_2$
$+ 5H_2O + 6NH_3$

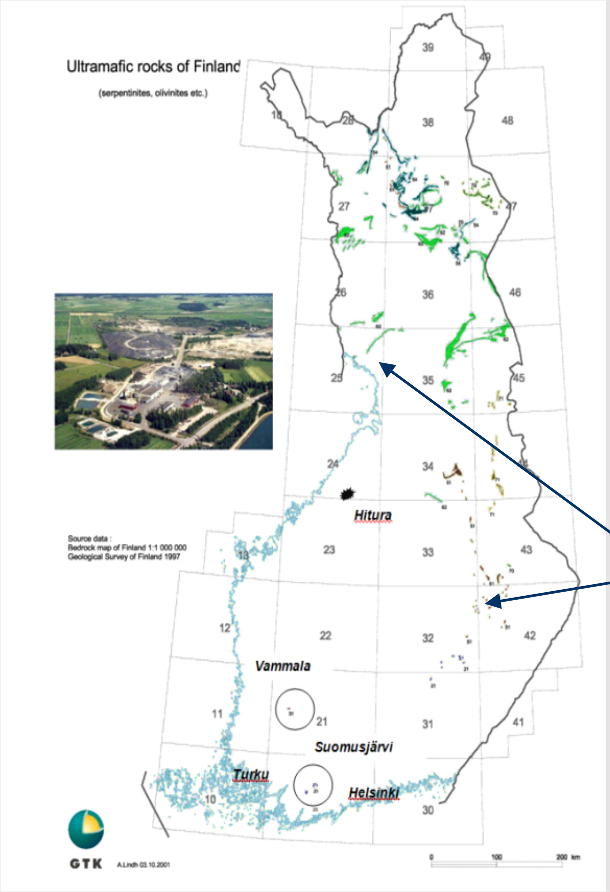
$MgSO_4$ + $3H_2O + 2NH_3 + CO_2$ (g)
←→ $(NH_4)_2SO_4$ + **$MgCO_3 \cdot 3H_2O$**
(optional: + heat 500°C)



http://dx.doi.org/10.2139/ssrn.4141031 (2021)

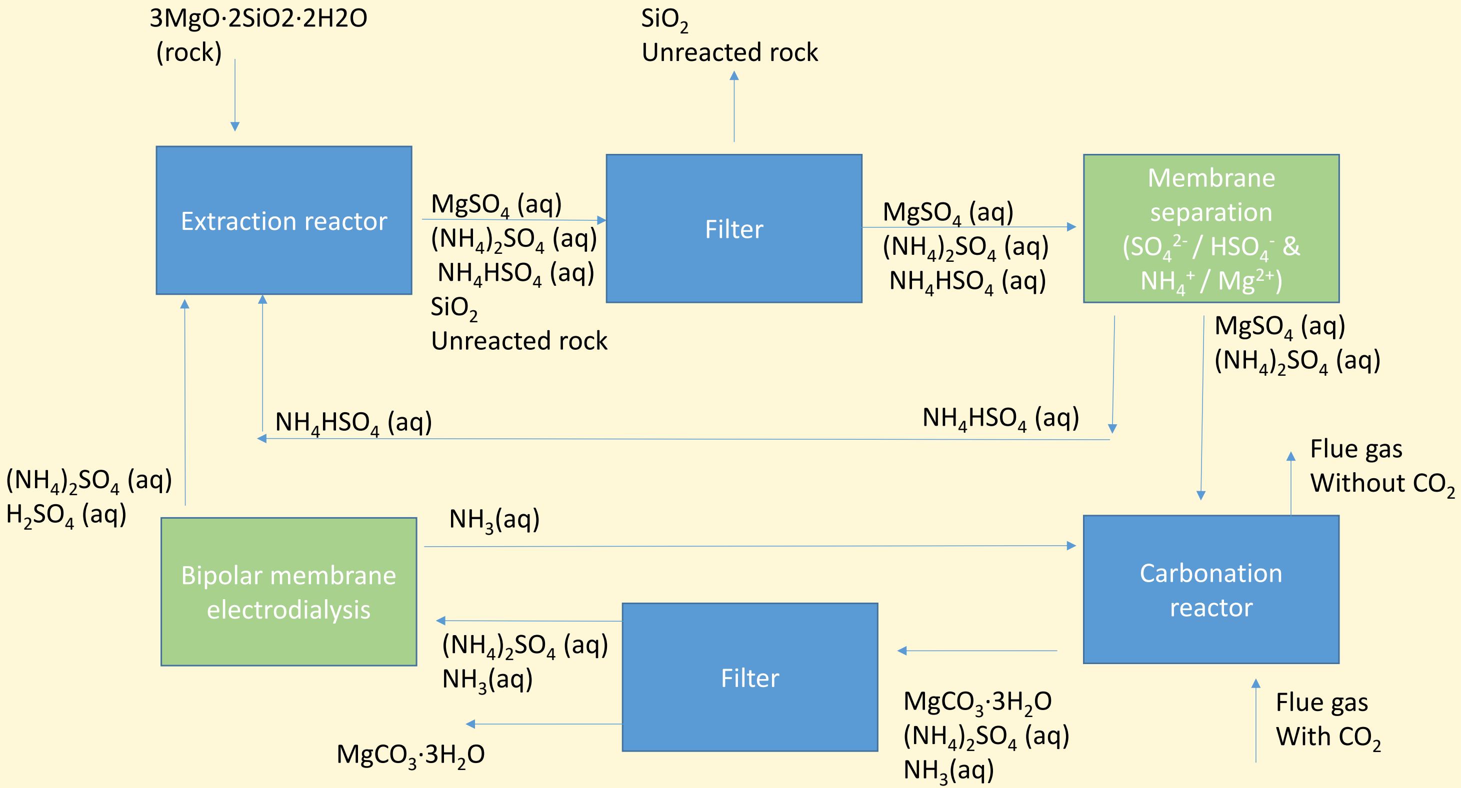
Finnish serpentinite

- $3MgO{\cdot}2SiO_2{\cdot}2H_2O + Fe_3O_4$ + traces of metal
- Less good: carbonate, calcium, too much metal. And asbestos-type material.
- Magnesium 20 ~ 25 %-wt



Current work

ÅA routes 3 & 4: membrane electrodialysis



http://dx.doi.org/10.2139/ssrn.4141031 (2021)

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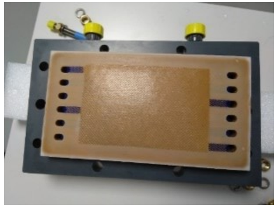
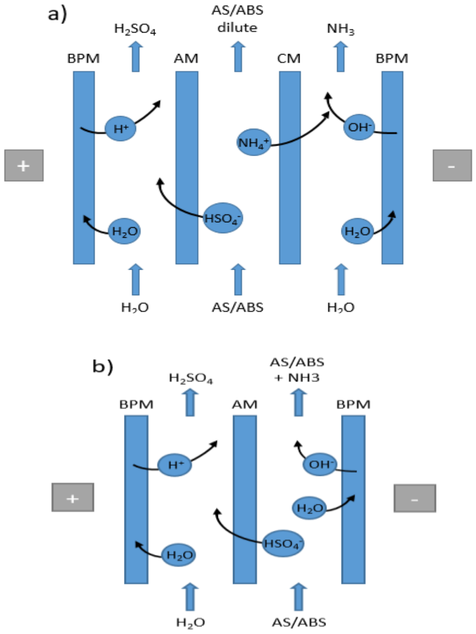
Naturvetenskaper
och teknik

CO_2 mineralization & membrane electrodialysis @ ÅA

2015 – 2019
Dr. thesis E Koivisto (2019)

2022 -





BPM = bipolar membrane
AM = anion selective membrane
CM = cation selective membrane
AS = ammonium sulphate
ABS = ammonium bisulphate

https://doi.org/10.1021/acsestwater.3c00028 (2023)

CO_2 mineralisation products

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- Nesquehonite $MgCO_3 \cdot 3H_2O$
- Magnesite $MgCO_3$

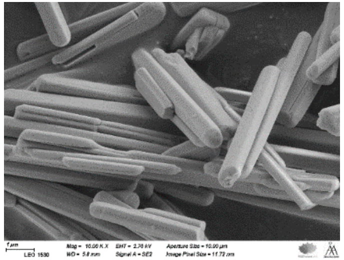
- Thermal energy storage (TES) 0 - 60°C

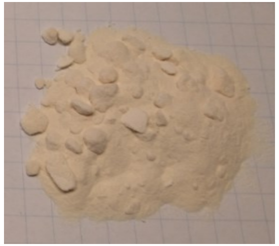
  $MgCO_3 \cdot 3H_2O$ + heat ←→ $MgCO_3$ + H2O (g)

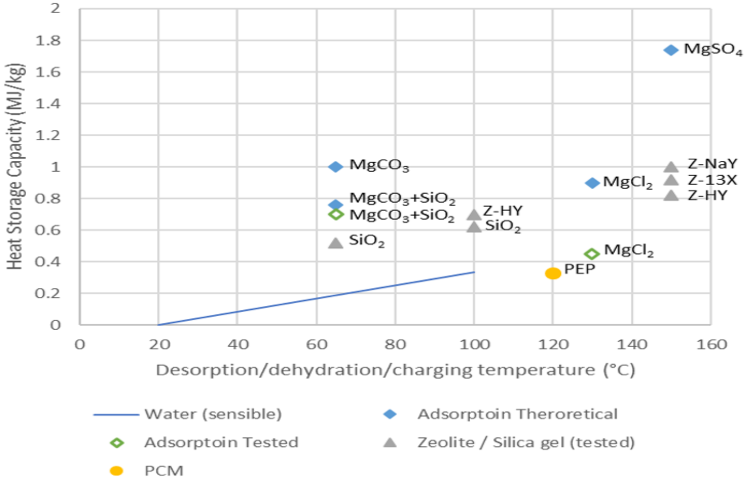
  heat effect ~ 1 MJ/kg

  (dr. thesis R. Erlund 2021)

- (Amorphous) quartz / sand
- Iron: Goethite FeOOH
- Other metals: Ni, Cu, Ti, Cr, ……







Project WPs interaction

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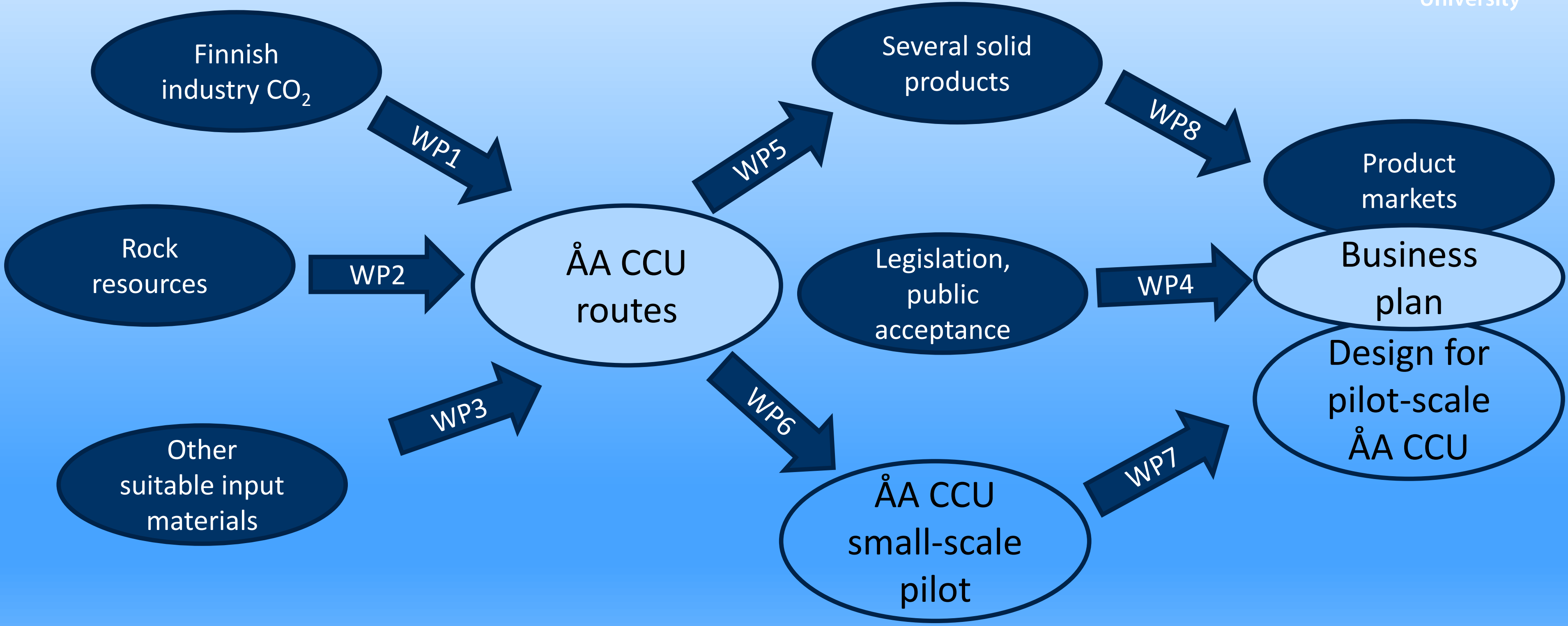

Results (PILCCU) so far

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- Finnish rock used for ÅA process development 2005-2020 no longer available ☹
- Outokumpu Chrome mining tailing may be a suitable feedstock but gives significant chrome oxide by-product amounts
- Elementis (talc producer) side-stone serpentinite may be suitable too
- Most likely ÅA route: aqueous processing using membrane-based process, operating on flue gas without CO_2 pre-capture
- Magnesium carbonate (hydrate), silica and metal products
- Process steps are optimised for integrated processing
- Social acceptance has been assessed with media analysis methods.
- Legislation on carbon capture and utilization (CCU) needs to be put in place. This needs proven stability and durability of carbonate product.
- Major milestone early 2024: demonstrating 100 kg/h CO_2 mineralisation @ Oulu Mining School

MAGNEX 2022-2025

Academy of Finland

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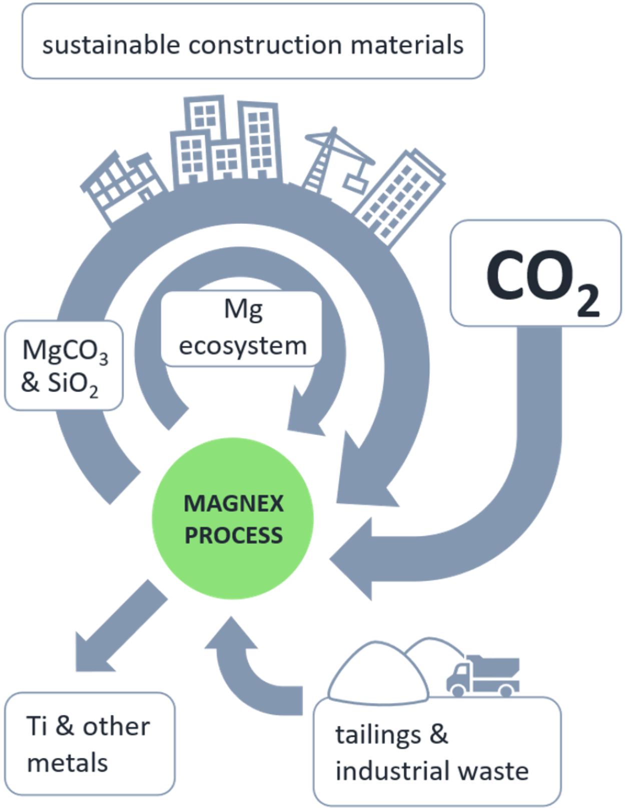

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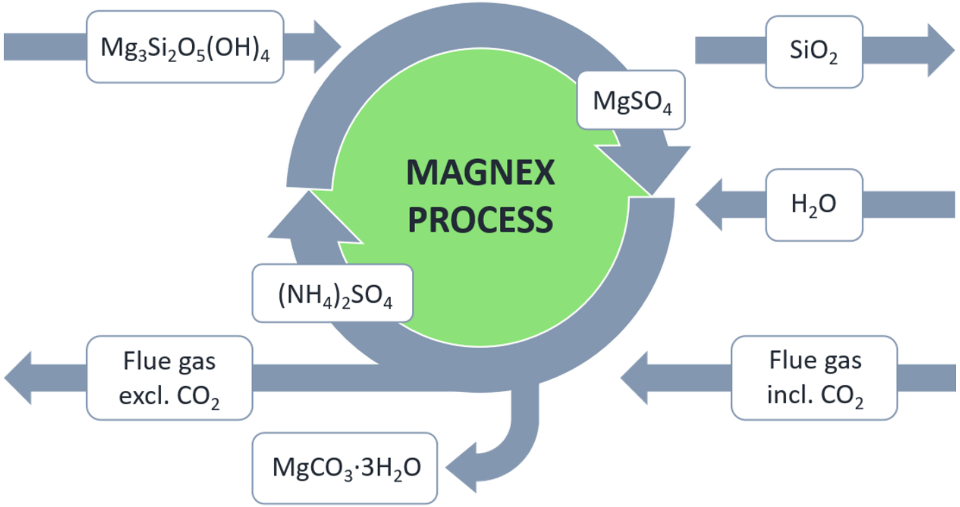
FIBRE AND PARTICLE ENGINEERING RESEARCH UNIT
UNIVERSITY OF OULU

Tampere University

Viable magnesium ecosystem: exploiting Mg from magnesium silicates with carbon capture and utilization

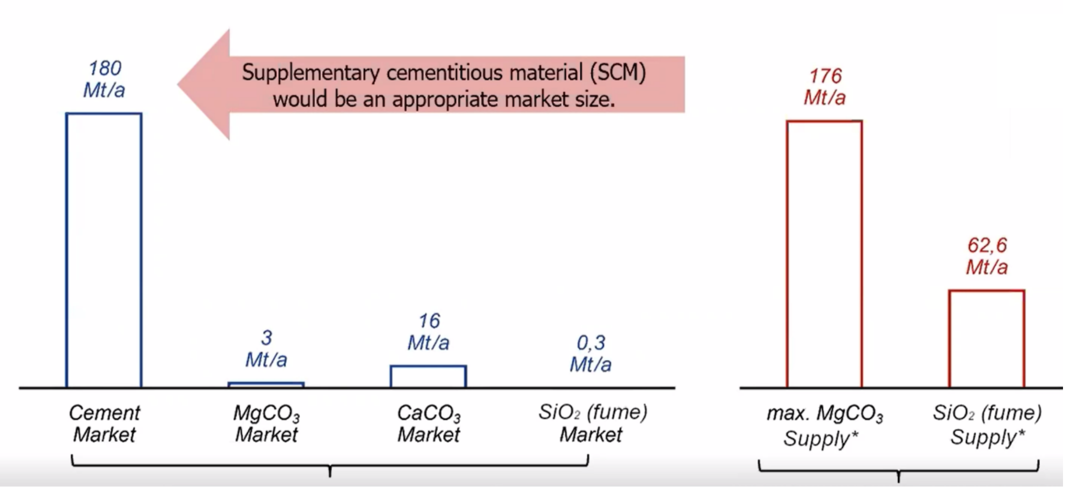
MAGNEX project



- **Main Aims:**
  - ✓ To improve the resource efficiency of the Mg-extraction process in the ÅA routes,
  - ✓ To accelerate the kinetics of Mg-carbonation,
  - ✓ To provide suitable applications for all generated material streams,

    and
  - ✓ To enable the Mg circular economy.

MAGNEX Motivations



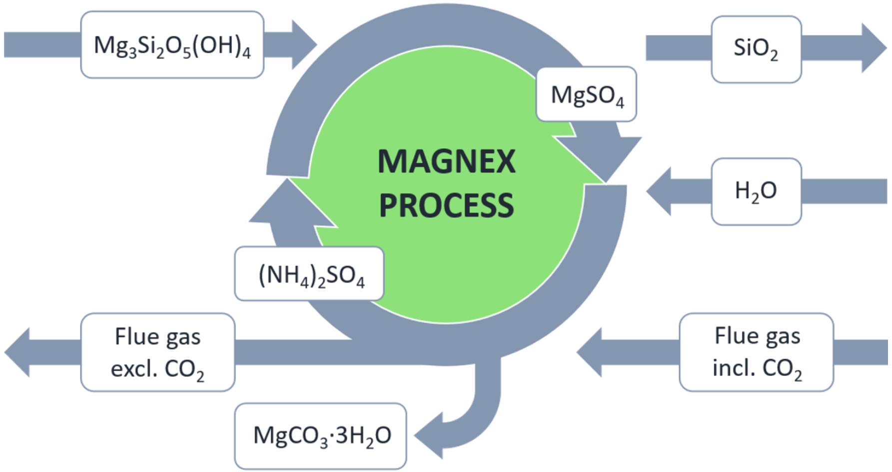
EU market size

Hypothetical production volume from Mg silicates

- Mg is a critical material for the EU industry, with primary supply from China (89%)
- Mg is the 8th most abundant element in Earth's crust: wide availability in brine, sea water and Mg-silicates
- Alternative routes to mining of Mg sources: electrodialysis or hydrometallurgical extraction
- Hydrometallurgical extraction: energy intensive, suffering from lack of scale

MAGNEX's Hypotheses

- **Hypothesis 1: Efficient extraction process**



- ✓ Mg-silicate feedstocks contain mainly silica (SiO_2(s)), critical (Mg, Ti, Nb, Bi, Be, Sb, Ge) and valuable metals (Fe, Cr, Ni) → electrodialysis and sequential processing steps can improve the recovery of process chemicals and enable additional purified products streams.
- ✓ Recovery of ammonium salts – electrodialysis membrane
- ✓ Recovery of additional metals - sequential selective precipitation steps with ion-selective membranes and careful pH control
- ✓ Recovery of silica – density based

Hypothesis 2. catalytic approach for $MgCO_3$ precipitation

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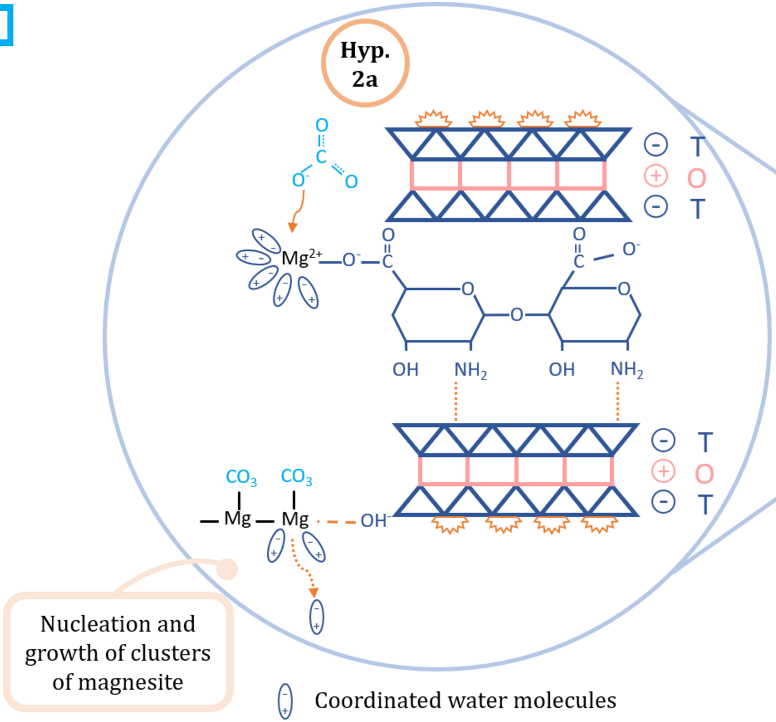


Coordinated water molecules

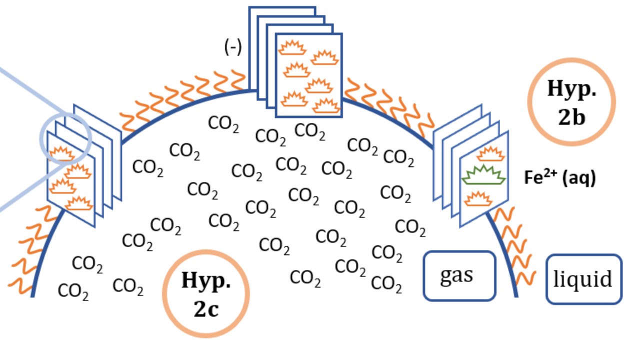
T Tetrahedral layers of smectite clays

O Octahedral layers of smectite clays

Multiple nucleation points

Effect on Fe^{2+} replacement on the crystal growth

Surfactant



Hyp. 2a Lowering the energy barrier for dehydration of $Mg^{2+}(H_2O)_6$ and facilitating the carbonation of Mg.

Hyp. 2b Lowering the stress of CO_3 groups via Fe^{2+} replacement in the magnesite crystal

Hyp. 2 c Maximized CO_2 gradient via formation of CO_2/water emulsions

Hypothesis 3. MAGNEX's applications and circularity

Fundamentals of the hypotheses:

- Optimizing the purity and the physico-chemical properties of the silicates and carbonate streams for high value (silica fume) and high-volume applications (construction)
- Deriving the parameters of the ÅA routes will allow recycling and upcycling industrial waste-streams

Hypothesis 4. Explotation of MAGNEX synergies

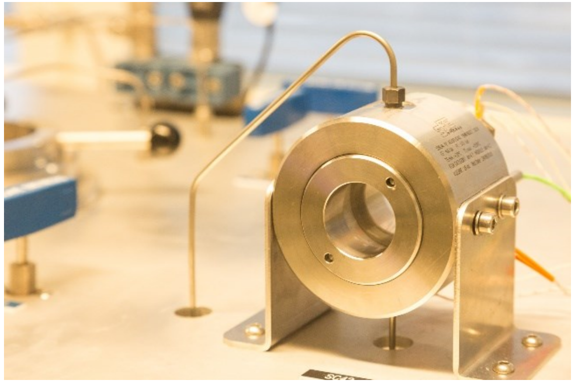
Fundamentals of the hypotheses:

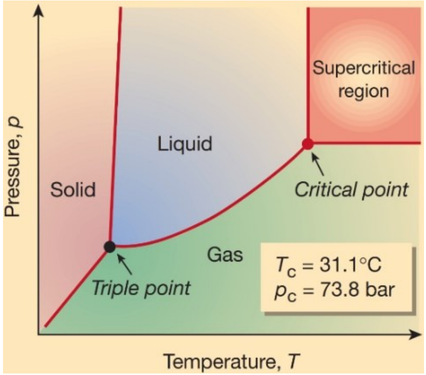
- The successful implementation of MAGNEX approach is dependant on technology and infrastructure development, legislation, market dynamics and the needs of stakeholders and government
- In order to introduce MAGNEX approach in the economy of the cities: assessment of costs, risks, liabilities and acceptance criteria, as well as to analyze the service and product-based business models

Routes for novel materials processing and acceleration of natural carbonation

Supercritical CO_2 equipment (1 of 2)

- Max pressure ~**350 bar**
- Max temperature +**100°C**
- Two separate reaction chambers
  - *Volume:* ***1.57 L***
  - *Width: 106 mm*
  - *Height: 268 mm*
- Co-solvent pump
- Analytic chamber with windows



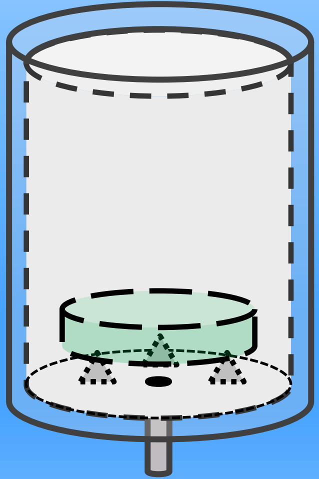


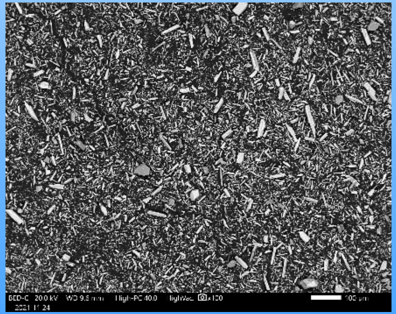
Case 1: Mineral carbonation 2021→

Accelerated weathering of silicates: from millennia to minutes

→ massive potential for immobilizing anthropogenic CO_2

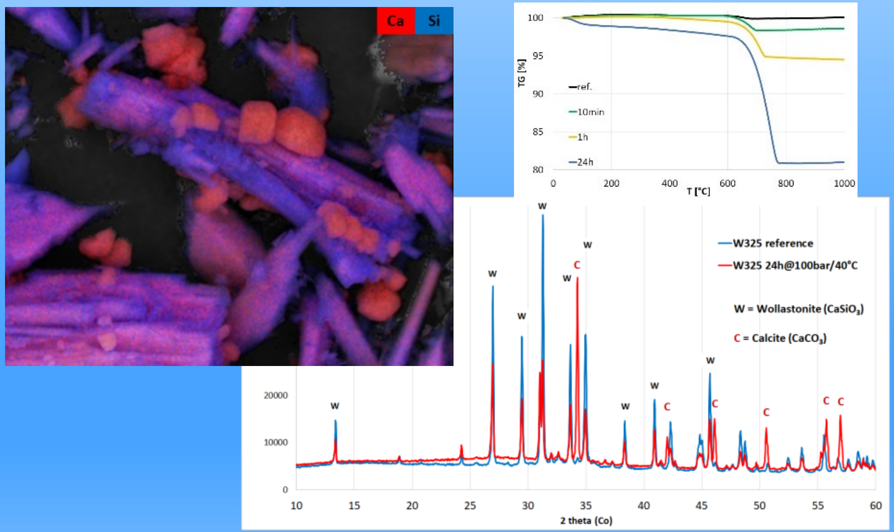
Batch-type (aqueous) pressurized CO_2 exposure





- Water + wollastonite
- Variables: t, P, T (10 min – 24 h, 20 – 100 bar, 40°C – 60°C)

Post-carbonation analysis: Qualitative (XRD,SEM) and quantitative (TGA)

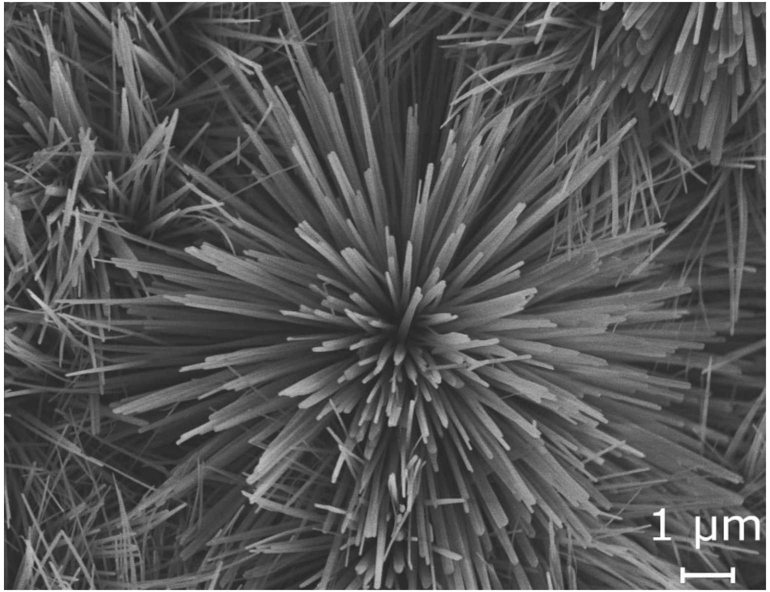


Case 2: Accelerated patination

(developed 2015-2021)

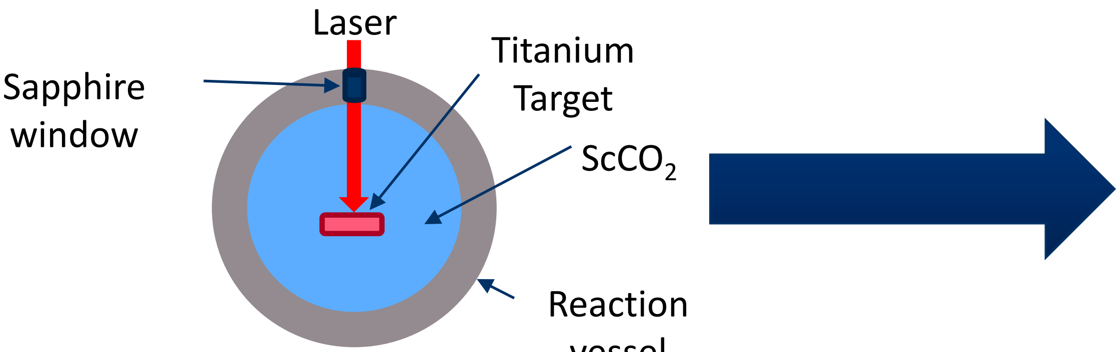
Nanorod formation on zinc with $ScCO_2$

Formation of carbonate nanostructures on zinc with $ScCO_2$. These nanostructures can be used to **improve corrosion resistance or paint adhesion** on galvanized steel sheets. These structures can be converted to **photocatalytic** zinc oxide surfaces by calcining.

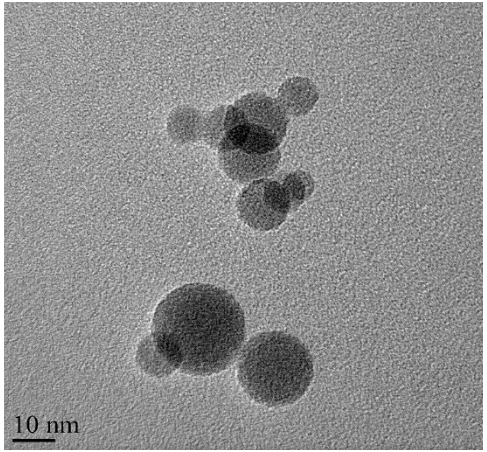


Case 3: Nanoparticle synthesis in $scCO_2$ by laser ablation (developed 2017-2021)

TiO_2 nanoparticles with high photocatalytic activity were produced by ablating a titanium target with laser in $scCO_2$. In addition to obtaining particles, the surface of titanium was functionalized by making it photoactive through formation of TiO_2 layer. Applications for photoactive materials include **solar cells**, **antimicrobial** and **self-cleaning** surfaces as well as **air- and water purification**.

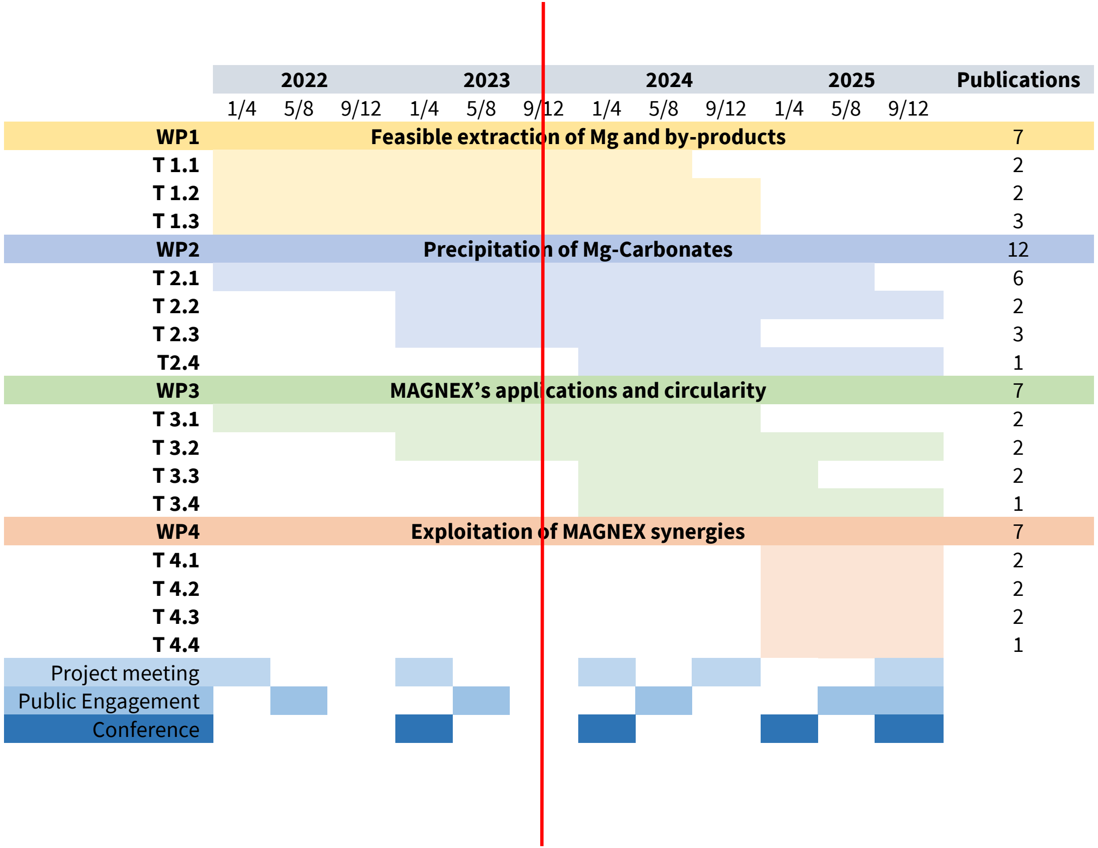


Schematic of synthesis procedure



TEM picture of TiO_2 nanoparticles

MAGNEX: Implementation



- Popular science articles and press releases
- Peer reviewed open access articles
- Articles in professional magazines
- Reporting at international conferences
- Industrial and academic networking

Results (MAGNEX) so far

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- Solid residues from Mg leaching from Mg silicate rock are being investigated for use as constructional materials
- The same applies to Mg carbonate (hydrate) product from carbonation
- Specific elecitricity consumption (SEC) of membrane electrolysis for flux salt recovery was improved x6 since early 2022
- Aqueous carbonation of Mg salts is slow: chemical kinetics understanding is increasing see also https://doi.org/10.1039/D2QI02482A (2023)
- Supercritical CO_2 carbonation tests on $Mg(OH)_2$ show significant effects of temperature, pressure and added water

Conclusions

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CO_2 mineralisation appears to be developing towards industrial scale deployment (TRL 5 → 9). Nonetheless: lab-scale R&D still needed. This includes non-technical barriers.

Circular economies and zero-waste concepts may result in society absorbing recycled / recovered materials

The MAGNEX and PILCCU projects benefit a lot from synergy and overlapping objectives

MAGNEX International Partners

- **Dr. Frank Winnefeld from EMPA (CH) -** complementary expertise in Mg- based binders, cement chemistry and thermodynamic modelling o
- **Prof. Martin Kunz (Advanced Light Source, Lawrence Berkeley Laboratory, Berkeley CA)** - Studies of the kinetics and mechanisms of the carbonation reactions utilizing the ALS beamline for in-situ synchrotron measurements.
- **Dr. Thierry Tassaing (CNRS Director of Research, University of Bordeaux, FR)** - In situ mineralization studies in $scCO_2$ with Raman and IR.
- **Dr. Inga Stasiulaitiene (University of Kaunas, LT)** - LCA studies under an Erasmus agreement.
- **Business Finland project PILCCU (Neste Veturi) synergy** and international partners (UK, Germany, South-Africa, Latvia)

The abstract....

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MAGNEX and PILCCU in Finland: deployment of CO_2 mineralisation in circular economies

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Two ongoing projects in Finland, MAGNEX (*Viable magnesium ecosystem: exploiting Mg from magnesium silicates with carbon capture and utilization*) and PILCCU (*Piloting of ÅA CCU*) aim at using CO_2 mineralisation technology for the overlapping purposes of large-scale CO_2 emissions mitigation and bringing several valuable material streams into circular economies, including construction. Of central importance are magnesium-based materials, such as magnesium carbonate hydrate (MCH), besides (amorphous) silica and several metallic species. On top of revenues from these, CO_2 emissions mitigation lowers the financial penalty from CO_2 emission rights under, for example, the European ETS.
The ÅA process routes are stepwise processes based on extraction of magnesium (and other species) from serpentinite-containing mining tailings from Finland, followed by precipitation of metallic species, carbonation using a CO_2 containing gas-stream (no separate capture step needed) and recovery of solvent salt, respectively.
Several separation steps involve (ion-selective) membrane electrodialysis. Besides ongoing mapping and characterisation of Finnish rock resources as tailings or other side-streams at metal and mineral mines in Finland, the projects address public acceptance, legislation and other non-technical issues related to large-scale roll-out of this type of CCU technology.
For the use of the solids, magnesium-based cement binders and plaster-like recipes are investigated as well as applications for the (amorphous) silica and other residues, including the use of MCH for cyclic thermal energy storage (TES). Special focus is on accelerating the carbonation step and the final outcome of MCH production, considering pressure (including supercritical CO_2 levels), and the role of recoverable catalysts and other additives.
The work receives funding from the Academy of Finland (2022-2025) and from Business Finland plus industry partners (2022-2024), respectively.