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Civil & Environmental Engineering

Low-temperature synthesis of portlandite for carbon dioxide mineralization

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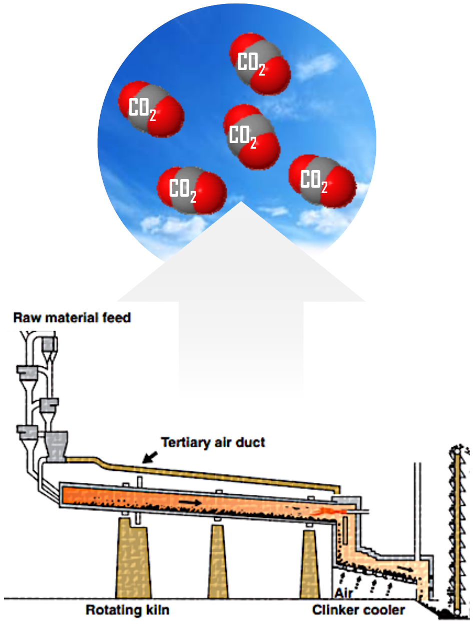
Carbon dioxide mineralization in concrete

- Concrete: 30 billion tons/year,[*] 4.1 billion tons of ordinary portland cement (OPC)[**]
- ~0.9 t CO_2 per t OPC[†]
- Energy input for processing at high temperature (~1600 °C) and CO_2 emission from calcination

$$CaCO_3 \rightarrow CaO + CO_2$$



OPC manufacturing

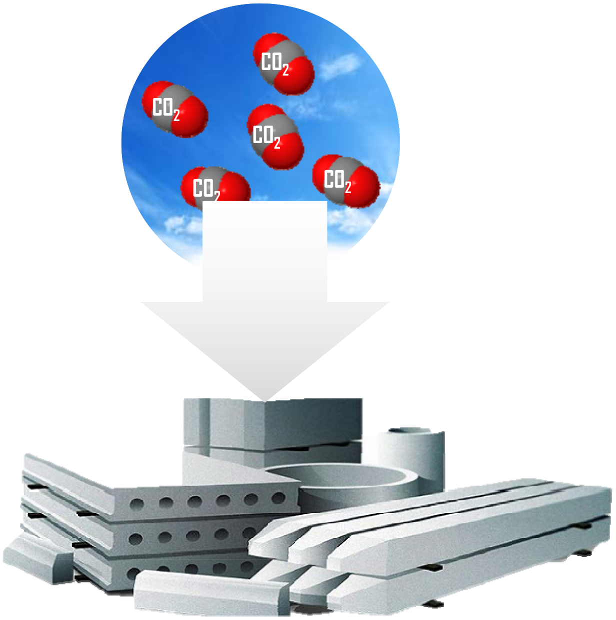
[*] Cement Sustainability Initiative, 2009; [**] USGS, 2018; [†] Gartner 2004

CO_2 mineralization to induce cementation

- Reaction of gaseous CO_2 with mineral phases to form solid products containing CO_2
- Ca- or Mg-containing minerals
- Stable Ca and Mg carbonates which bind aggregates
- Dissolution–precipitation

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2$$



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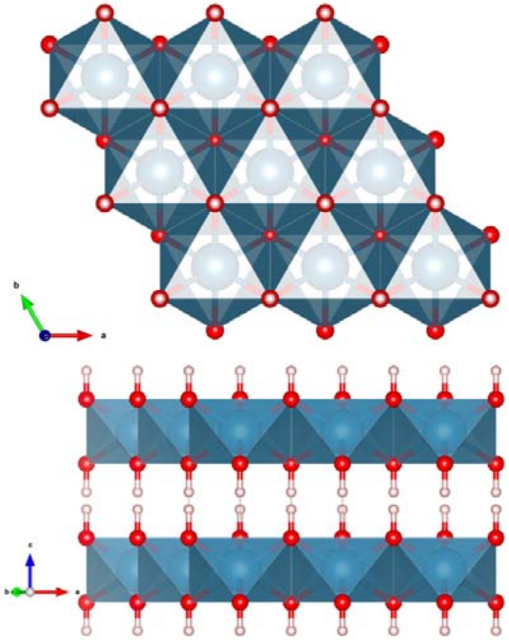
Calcium hydroxide (portlandite)

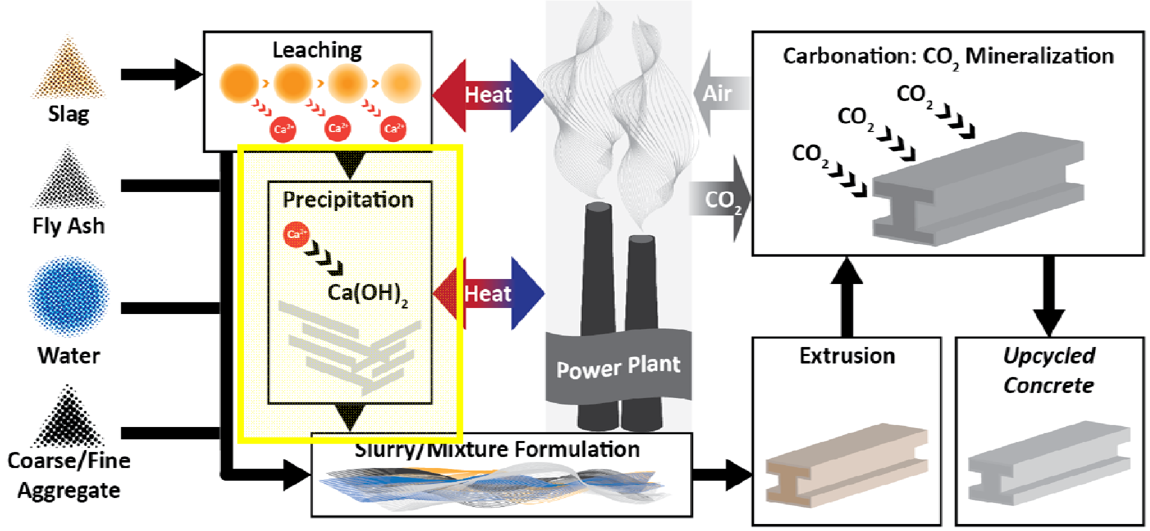
- Hydrated lime is an efficient material for CO_2 uptake (max. <u>59%</u> by mass)

$$\mathbf{Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O}$$

- Industrial method of production require energy-, CO_2-intensive calcination
- Here, low-temperature synthesis of portlandite using industrial by-products and waste heat

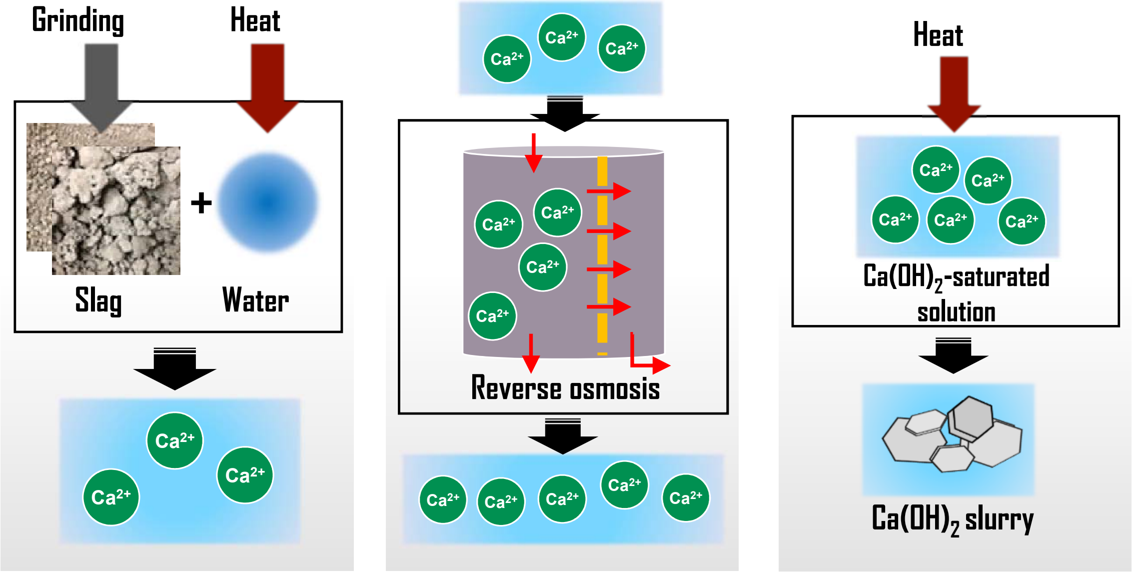


Upcycled concrete production



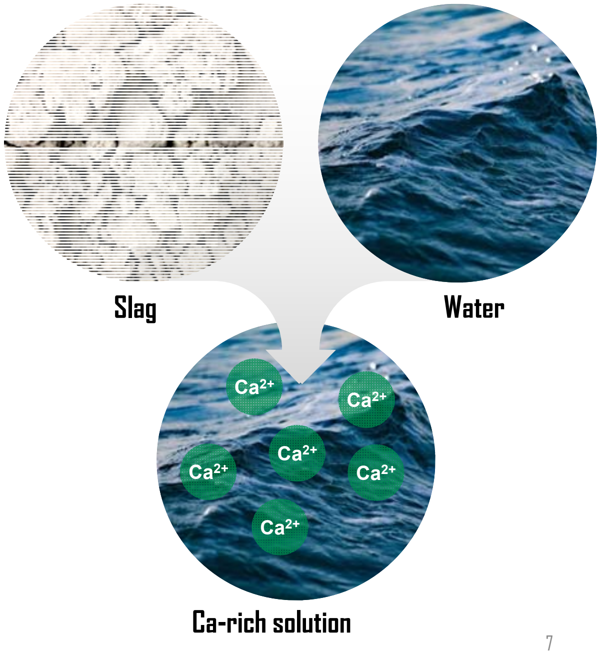
Slag
Fly Ash
Water
Coarse/Fine Aggregate
Leaching
Ca^{2+}
Heat
Precipitation
Ca^{2+}
$Ca(OH)_2$
Heat
Slurry/Mixture Formulation
Power Plant
Air
CO_2
Carbonation: CO_2 Mineralization
CO_2
CO_2
CO_2
Extrusion
Upcycled Concrete

Synthesis of calcium hydroxide



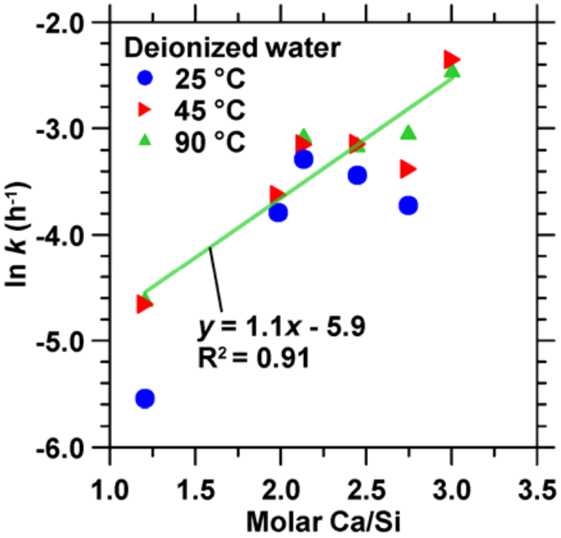
Sourcing calcium from slags

- Slags contain about 30–50% CaO by mass; Ca: ~0.2–0.3 g per g slag
- Crystalline slags used as low-value aggregates the target of this process
- Rapidly evolves to a highly alkaline solution amenable to portlandite precipitation (final step)



Kinetics of aqueous Ca extraction

- Up to 10 mM (400 ppm) Ca leached in water after 24 h
- Rate constants, *k*, derived by fitting $X_{Ca} = kt^{\alpha}$, where $X_{Ca} = \frac{m_{Ca,t}}{m_{Ca,t_n}}$ and $m_{Ca,t}$ and m_{Ca,t_n} are the total mass of Ca dissolved at time, *t* and at completion, and α is the apparent reaction order
- Analysis reveals effects of processing conditions and slag type



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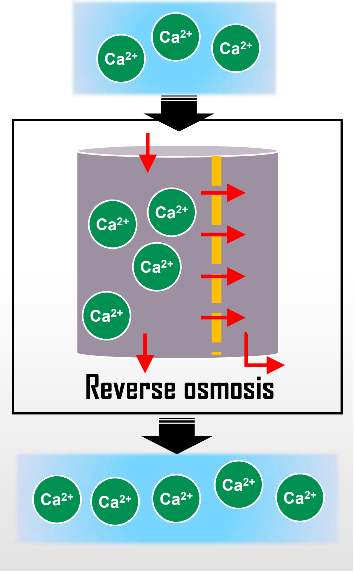
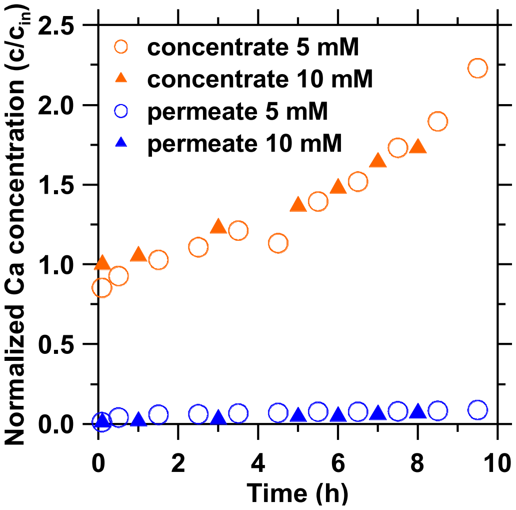
Increasing [Ca] to reach $Ca(OH)_2$ saturation

- Nanofiltration and reverse osmosis (RO) membranes to concentrate solutions containing ~5-10 mM $Ca(OH)_2$
- Dow Filmtec® NF90 nanofiltration (200–400 Da) or BW30XFR RO (100 Da)
- Polyamide-thin film composite
- pH range = 2–11 or 2–12
- Salt rejection: 97% $MgSO_4$ or 99.7% NaCl



Concentration of $Ca(OH)_2$ solutions

- Ca concentration factor up to >2x using RO membrane (vs. <1.2x using nanofiltration)
- RO showed greater Ca rejection (>98%) than nanofiltration (<20%)
- RO suitable for concentration of alkaline Ca-rich solutions
- Operating pressure: 50–60 psi



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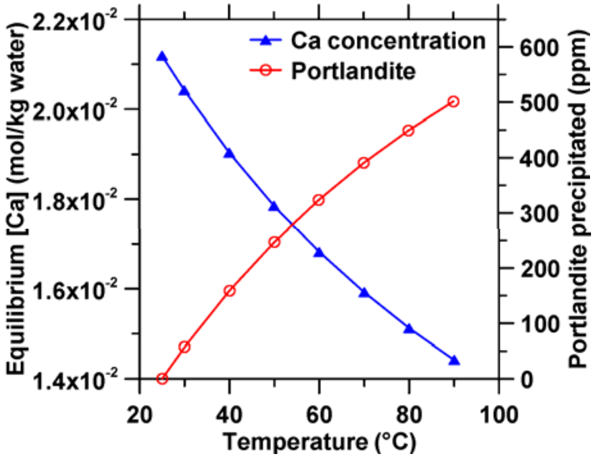
Temperature ramping for precipitation

- Portlandite solubility decreases with increasing temperature
- Up to 500 ppm can be precipitated from a saturated solution
- pH adjustment not needed because slag leachate is alkaline



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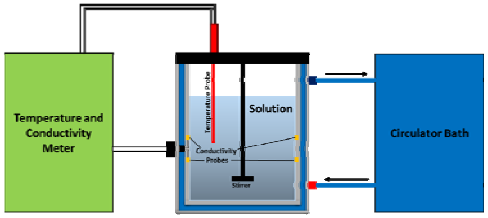
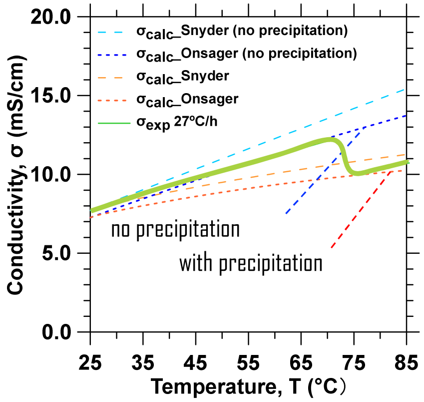
Precipitation kinetics of portlandite

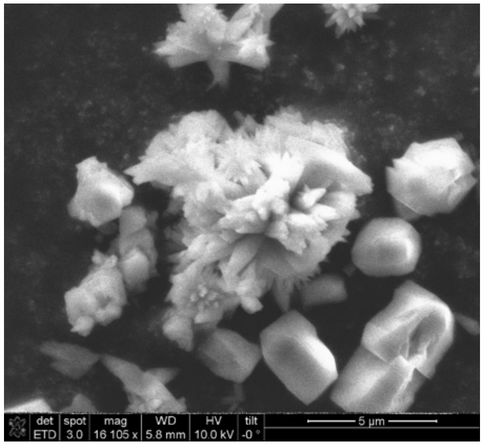
- ➢ $Ca(OH)_2$-saturated solutions ([Ca]=21 mM) in a batch reactor
- ➢ Temperature ramped up from 25 to 85 °C at different rates
- ➢ Portlandite precipitation initiates at ~55–65 °C, depending on ramp rate
- ➢ Ongoing studies on controls on kinetics (e.g., induction time, ΔG, continuous stirred-tank reactors)





Summary: Low-temperature synthesis

- ➢Crystalline slags dissolve sufficiently – up to 10 mM Ca after 24 h
- ➢RO membrane filtration enable concentration of alkaline Ca-rich solutions
- ➢Precipitation via temperature ramping occurs rapidly starting at T ~ 55 †C
- ➢***Energy consumption? Implementation at a laboratory or industrial scale?***



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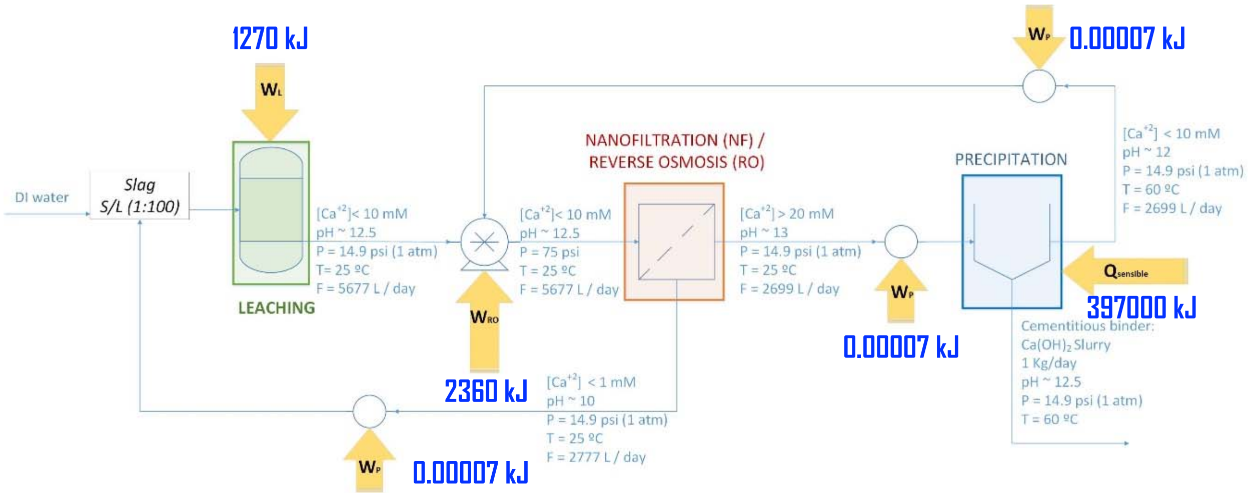
Energy consumption per kg $Ca(OH)_2$

- ➢Total is ~3630 kJ/kg (excluding $Q_{sensible}$), similar to theoretical energy for calcination-based synthesis



1270 kJ

W_L

DI water

Slag
S/L (1:100)

LEACHING

$[Ca^{+2}]$< 10 mM
pH ~ 12.5
P = 14.9 psi (1 atm)
T= 25 ºC
F = 5677 L / day

W_{RO}

2360 kJ

NANOFILTRATION (NF) /
REVERSE OSMOSIS (RO)

$[Ca^{+2}]$< 10 mM
pH ~ 12.5
P = 75 psi
T = 25 ºC
F = 5677 L / day

$[Ca^{+2}]$ > 20 mM
pH ~ 13
P = 14.9 psi (1 atm)
T = 25 ºC
F = 2699 L / day

W_P

0.00007 kJ

$[Ca^{+2}]$ < 1 mM
pH ~ 10
P = 14.9 psi (1 atm)
T = 25 ºC
F = 2777 L / day

W_P

0.00007 kJ

PRECIPITATION

$Q_{sensible}$

397000 kJ

W_P

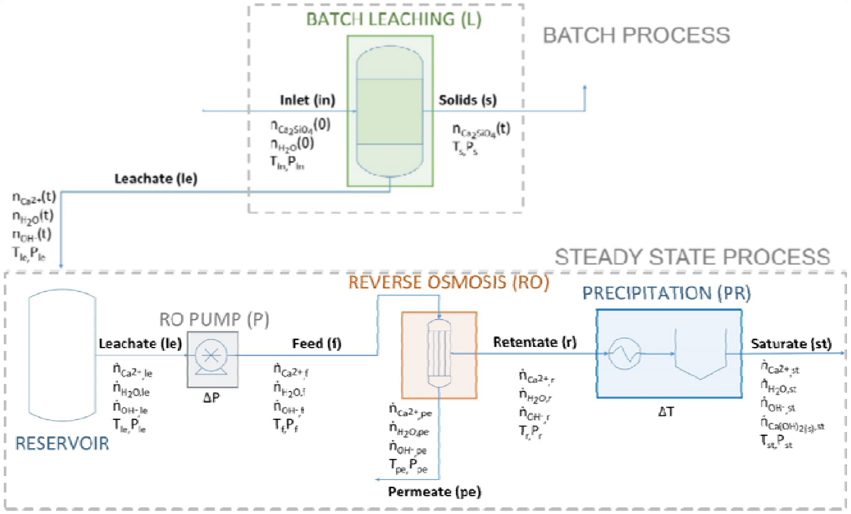
0.00007 kJ

$[Ca^{+2}]$ < 10 mM
pH ~ 12
P = 14.9 psi (1 atm)
T = 60 ºC
F = 2699 L / day

Cementitious binder:
$Ca(OH)_2$ Slurry
1 Kg/day
pH ~ 12.5
P = 14.9 psi (1 atm)
T = 60 ºC

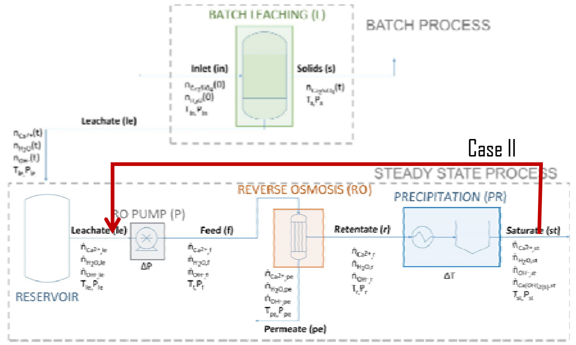
Process simulations using Aspen Plus™

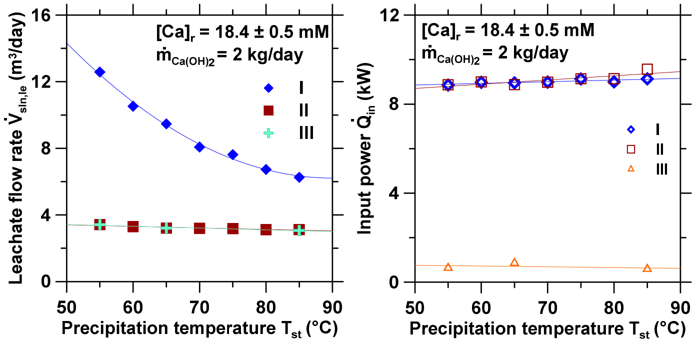
- Minimize precipitation power at fixed $Ca(OH)_2$ throughput
  - Water recirculation
  - Heat recovery
- Minimize water consumption & pumping power at fixed precipitation power



Minimization of precipitation power

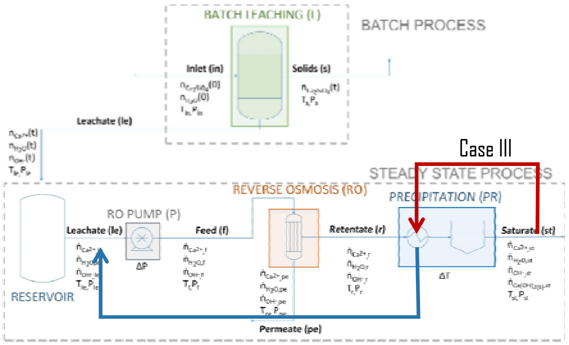
- Increasing T decreases water consumption (Case I)
- Recirculation of precipitation filtrate as RO feed ([Ca]: 10–13 mM) –Reduced water consumption (Case II)
- $\dot{W}_e$ constant for variable T (lower T_{st} results in higher [Ca] in recirculate)
- Input power largely unaffected by water recirculation

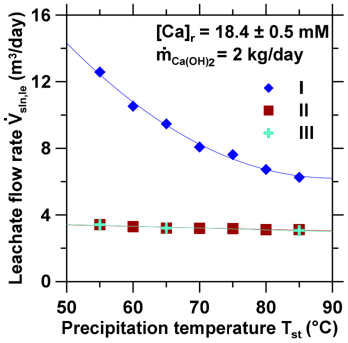


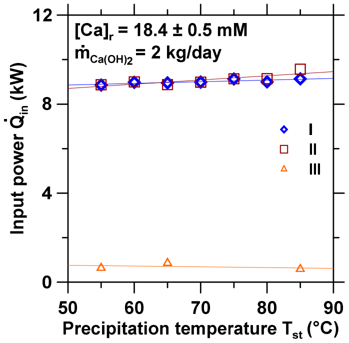


Process optimization and heat integration

- Precipitation power, $\dot{Q}_{pr} = \dot{Q}_{in} + \dot{Q}_{re}$, where $\dot{Q}_{in}$ is the input from a waste heat and $\dot{Q}_{re}$ is from heat recovery
- Utilize heat of recirculated saturate (Case III)
- Heat recovery does not affect water consumption and pumping power (compare with Case II)
- Significantly reduced $\dot{Q}_{in}$

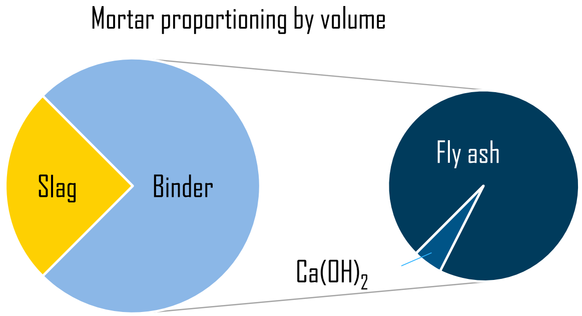






CO_2 emissions reduction of $Ca(OH)_2$ mortars

- ➢ CO_2 emissions for $Ca(OH)_2$ calculated based on pumping energy
- ➢ 0.81 kWh/kg $Ca(OH)_2$ using a pump efficiency of 80%, or 0.4 kg CO_2/kg $Ca(OH)_2$



- ➢ CO_2 emissions of 38 kg CO_2/m^3 (vs. OPC-based concrete: 300.6 kg CO_2/m^3), results in CO_2 emissions reduction of 75%
- ➢ Assuming a CO_2 uptake of 5% by mass of solids, CO_2 emissions reduction increases to 120%

Conclusions

- Low-temperature synthesis of portlandite envisioned to employ waste heat from a power plant (flue gas, blowdown steam)
- Considering pumping power only, new process features lower energy requirement than typical industrial process
- Additional strategies to reduce water use include: permeate recycling to leaching reactor, and utilization of moisture from blowdown steam
- Precipitated portlandite mixed within net CO_2-negative concrete

Acknowledgements

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