Fine Calcium Carbonate Production by CO$_2$ Mineralization of Industrial Waste Brines

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Carbon Utilization
Need global strategy for carbon management

>36 Gt CO₂ emitted globally per year

...Need to remove 10-20 Gt CO₂ per year

...5.5 Gt of C per year
Current models of carbon management

- **CCS**
  - 22,000 Gt potential capacity (North America)
  - Limited to ~1,000 Mt CO₂/year
  - Risk of CO₂ migration and leakage

- "Recycled" CO₂
  - Potentially profitable for businesses
  - Need for co-feed molecules
  - Displaces only ~30% need
    - Gasoline in the US would only account for 7% of need
Thermodynamic, Kinetic, and Political Barriers

0.11 kWh per kg CO₂ for optimum Amine unit
>390 kJ/mol CO$_2$ to overcome rxn energy

>415 kJ/mol average C-H BDE of methane
Thermodynamic, Kinetic, and Political Barriers

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Can we develop additional processes with less severe science and engineering hurdles?
Alternative Processes for Precipitated Calcium Carbonate Production

A synthetic analogue of natural process

- CO₂ fixed within stable mineral carbonates, mimicking the natural process of biogenic abiogenic limestone formation
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- Thermodynamically favorable
A synthetic analogue of natural process

- $\text{CO}_2$ fixed within stable mineral carbonates, mimicking the natural process of biogenic/abiogenic limestone formation.
- Thermodynamically favorable.
- Utilizes abundant and/or waste sources of Ca.

Seawater, Desalination Brines, Industrial Wastewater, Produced Water.

\[ \Delta G_f^0 \text{ (kJ/mol)} \]

- $-394$ for $\text{CO}_2$
- $-295$ for $\text{HCOOH}$
- $-361$ for $\text{H}_3\text{CCOOH}$
- $-382$ for $\text{H}_2\text{O}$
- $-51$ for $\text{CH}_4$
- $-4$ for $\text{C}_6\text{H}_{14}$

$\text{Ca}^{2+} (\text{aq})$
A synthetic analogue of natural process

- CO₂ fixed within stable mineral carbonates, mimicking the natural process of biogenic or abiogenic limestone formation.
- Thermodynamically favorable.
- Utilizes abundant and/or waste sources of Ca.
- Economically competitive and environmentally "friendlier" process.
Precipitated Calcium Carbonate Processes

**Current Process**

- Quarried Crushed Limestone: 1.12 ton ($13.70)
- Water: 6.0 ton ($15.0)
- CO₂: 0.21 ton
- Fossil Fuel for heating: 3750 MJ, 130 kg Coal ($7.80)
- Electricity: 277 kWh ($25)
- CaCO₃: 1 ton ($340)
- Residue: 0.09 ton ($13.70)
- Production Cost: $15.00
Precipitated Calcium Carbonate Processes

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- Quarried Crushed Limestone: 1.12 ton ($13.70)
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**CO\(_2\) Mitigation**
- CO\(_2\): 0.4 ton ($0)
- Reduced energy/emissions
- Wastewater: 40,000 ton ($0)

**Alternative Process**
- CaCO\(_3\): 1 ton ($340)
- Residue: 0.09 ton
- Electricity: 332 kWh ($30)
- No emissions

**Mitigates waste handling costs**
Alternative Processes for Precipitated Calcium Carbonate Production

**Current Process**

- 0.21 ton CO$_2$
- Quarried Crushed Limestone
- Water
- Fossil Fuel for heating
- No emissions
- 1 ton CaCO$_3$
- 0.4 ton CO$_2$ ($0)
- 40,000 ton ($0)
- 332 kWh
- Residue 0.09 ton
- Wastewater 1.12 ton ($13.70)
- 6.0 ton ($15.0)
- Electricity 277 kWh, 3750 MJ
- 130 kg Coal ($7.80) ($25)

**Alternative Process**

- Mitigates waste handling costs
- Reduced energy/emissions
- Potential $10 Billion increase in market Value
- CaCO$_3$ 1 ton ($340)
- Residue 0.09 ton
- Wastewater 40,000 ton ($0)
- Energy 332 kWh ($30)
Different thermodynamic barrier

- Alkalinity must be supplied to continuously precipitate CaCO$_3$

- Inducing alkalinity with consumable bases (e.g., NaOH) is expensive and energy intensive

\[
\text{Ca}^{2+} \text{(aq)} + \text{CO}_2 \text{(g)} + \text{H}_2\text{O} \text{(l)} \rightarrow \text{CaCO}_3 \text{(s)} + 2\text{H}^+ \text{(aq)}
\]
Alternative Processes for Precipitated Calcium Carbonate Production

Different thermodynamic barrier

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- Ion-exchange materials may be an attractive, reusable alternative
Proposed process integrating ion-exchange

- Ion exchange reactor may be constructed in the form of packed columns (grain size considerations)
- Acidity is induced by CO₂ dissolution, ion-exchange produces a CO₃²⁻-rich solution
- Reaction of CO₃²⁻-rich solution with Ca²⁺-rich produced water forms calcite
- Ion-exchanger regenerated using Ca-depleted produced water
Proposed process integrating ion-exchange

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- Acidity is induced by CO$_2$ dissolution, ion-exchange produces a CO$_3^{2-}$-rich solution
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What ion exchange materials deliver desirable exchange capacity, dynamics, and stability?
Regenerable ion-exchangers

- Natural materials such as phyllosilicates (layered silicates/clays) and zeolites, and synthetic resins can be used as ion-exchangers
- Compare based on capacity for and kinetics of ion exchange and for stability/extent of regeneration
Na⁺/H⁺ exchange using resins, clays, zeolites

- Batch experiments: bubble CO₂ into DI water until pH 4, then add ion exchanger and observe pH increase
- Two zeolites and two resins meet the “minimum” requirement of pH > 8
**Na⁺/H⁺ exchange using resins, clays, zeolites**

- Batch experiments: bubble CO₂ into DI water until pH 4, then add ion exchanger and observe pH increase.

- Two zeolites and two resins meet the “minimum” requirement of pH > 8.

- Na⁺ release appears to be unbalanced but follows the same trend as pH increase.
Exchange Isotherms point to the resins and 4A
Dynamics of zeolites

- No diffusion restrictions on exchange equilibrium
- Microporous structure may slow uptake kinetics (larger process vessel)
• Achieve equilibrium exchange capacities; Faster uptake kinetics
• Still observe a pH increase from 4 to 7
• Shift in breakthrough not proportional with contact time
Precipitation using column effluent

- CaCO$_3$ precipitation (XRD) following column ion exchange (using 0.10 M CaCl$_2$)
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**Precipitation using column effluent**

- **CaCO$_3$ precipitation (XRD) following column ion exchange (using 0.10 M CaCl$_2$)**

- Achieve (close to) the thermodynamic maximum amount of CaCO$_3$ (using PHREEQC minteq database)

- Small reaction time length or loss of CO$_2$ may explain differences in calculated and experimental CaCO$_3$ (s) values
Precipitation using column effluent

Known zeolites and resins can achieve thermodynamic maxima for overall process

- Achieve (close to) the thermodynamic maximum

Regeneration? Higher than expected Na\(^+\) during batch exchange? Post-breakthrough pH = 7?

Small reaction time length or loss of CO\(_2\) may explain differences in calculated and experimental CaCO\(_3\) (s) values
FTIR characterization of organic ion exchange resins

- TP-260: Loss of amino methyl phosphonic acid after exposure to water at pH = 11.8

![FTIR spectrum](image)
FTIR characterization of organic ion exchange resins

- TP-260: Loss of amino methyl phosphonic acid after exposure to water at pH = 11.8

$$\text{H}_2\text{N}-\overset{2}{\text{O}}-\text{P}^\text{1}-\overset{3}{\text{OH}}$$

- 200C: Loss of sulfonic acid functional group

$$\text{O=S=O}$$

$$\text{O}$$
FTIR characterization of organic ion exchange resins

- TP-260: Loss of amino methyl phosphonic acid after exposure to water at pH = 11.8

Leaching of active sites on resin materials introduces Na\(^+\) into solution and can titrate protons
Conclusions

• Production of precipitated calcium carbonate using industrial waste brines presents substantial reductions in GHG emissions

• Various pathways have been identified, processes need to be characterized and controlled

• Ion-exchange produces a $\text{CO}_3^{2-}$-rich solution, Reaction of $\text{CO}_3^{2-}$-rich solution with $\text{Ca}^{2+}$-rich produced water forms calcite

• Resins exhibit higher “capacity” and better kinetics, but are unstable in water at low pH
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