Chemical CO$_2$ Mitigation: An Option for the Cement Industry

Greg H. Rau
Institute of Marine Sciences
University of California, Santa Cruz
And
Carbon Management Program
Energy and Environmental Security Div.
Lawrence Livermore National Laboratory

rau4@llnl.gov

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The chemical reactivity of CO$_2$ with hydroxide or carbonate solutions can be exploited for low-cost, low-tech CO$_2$ mitigation.

As an example, the waste metal oxides produced in cement manufacture (cement kiln dust) can be hydrated and used as a CO$_2$ absorber, with other potential co-benefits.
The chemical reactivity of CO$_2$ can be used for CO$_2$ mitigation:

- CO$_2$ is a reactive compound, e.g.:
  - CO$_2$ + OH$^-$ $\rightarrow$ HCO$_3^-$
  - CO$_3^{2-}$ + H$_2$O $\rightarrow$ 2HCO$_3^-$
  - MO $\rightarrow$ MCO$_3$
  - M$^0$ + H$_2$O $\rightarrow$ MCO$_3$ + H$_2$

- Requirements for cost-effective, safe sequestration:
  - Low energy input
  - Inexpensive, abundant reactants
  - Benign, storable/useable products
Nature’s Chemical CO$_2$ Capture and Storage:

Nature’s own mechanisms:

Atmospheric CO$_2$

- **Photosynthesis**
  
  $\text{CO}_2 + \text{H}_2\text{O} + \text{photons} \rightarrow R-(\text{CH}_2\text{O}) + \text{O}_2$

- **Ocean uptake**
  
  $\text{CO}_2 + \text{H}_2\text{O} + \text{CO}_3^{2-} \rightarrow 2\text{H}^+ + 2\text{HCO}_3^-$

**Weathering Reactions**

- **Silicate weathering**: $\text{CO}_2 + \text{Ca/MgOSiO}_2 \rightarrow \text{Ca/MgCO}_3 + \text{SiO}_2$
- **Carbonate weathering**: $\text{CO}_2 + \text{H}_2\text{O} + \text{CaCO}_3 \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$
Natural CO$_2$ Sequestration: Effective but slow

Instantaneous doubling of pre-industrial atmospheric CO$_2$ content

Equilibration of atmosphere with mixed-layer

Mixing between surface ocean and deep ocean

Carbonate dissolution

Silicate-rock weathering

(Caldeira and Rau, 2000)
Accelerated Weathering of Limestone (AWL) Reactor:

(Rau and Caldeira, 1999)
Analogies to Flue Gas Desulfurization:

**AWL:**

\[ \text{CO}_2(g) + \text{H}_2\text{O}(l) + \text{CaCO}_3(s) \rightarrow \text{Ca}^{2+}(aq) + 2\text{HCO}_3^-(aq) \]

**FGD:**

\[ \text{SO}_2(g) + \text{H}_2\text{O}(l) + \text{CaCO}_3(s) \rightarrow \text{CaSO}_3(aq) + \uparrow\text{CO}_2(g) + \text{H}_2\text{O}(l) \]

\[ \text{CaSO}_3(aq) + 0.5\text{O}_2 \rightarrow \downarrow\text{CaSO}_4(s) \]

➤ Gases captured via reaction with wet limestone (at ambient temperature and pressure), and converted to benign, storable/useable liquids or solids

**AWL cost:** $3-$30/tonne CO\textsubscript{2} avoided
**CO₂ Mitigation In Cement Manufacture:**

CCAP Report 2005: CA Cement Manufacture -

- Current state emissions $\approx 10.5$ MMT CO₂/yr
  - Flue gas is 20-30% CO₂
- Est. BAU emissions in 2020 = 13.6 MMTCO₂/yr
- Might be reduced to 11 MMTCO₂/yr by 2020 at a cost <$10/tonne CO₂ via:
  - Limestone or flyash + cement blends
  - Alternative fuels
- But AB 32 mandates state return to 1990 emissions (CA cement, est. 7.8 MMTCO₂/yr) by 2020
- Therefore, current CO₂ reduction path inadequate.
Chemical Composition of CKD:

- Strongly alkaline waste (pH > 12); highly reactive with acid gases including CO₂
- Quantity of waste CKD produced per tonne clinker quite variable: 0 to >25%.
- However, legacy CKD stockpile is massive
  - 82,000 tonnes/yr disposed of in California alone (‘05 PCA Survey)
  - 3.3 MMT disposed nationally in US in 1995, 4 MMT in 1990 (EPA)

### US Mitigation potential: 3 MMT CKD X 50 years X 0.5 T CO₂ /T CKD = 75 MMT CO₂
Use Highly Alkaline Waste Cement Kiln Dust for CO₂ Mitigation:

CaCO₃ + sand + high heat → Kiln → cement

CO₂ and Kiln Dust Mitigation in Cement Manufacture

CO₂ → alkaline cement kiln dust (CKD) → pH>12 → Aqueous CO₂ + CKD contactor

e.g., Ca(OH)₂ + 2CO₂ → Ca²⁺ + 2HCO₃⁻

Settling/precipitation reservoir(s)

Ca²⁺ + 2HCO₃⁻ → C

Na,K,Mg Carbonates

<--CaCO₃ recycle -and/or- sequestration as CaCO₃

Air
Air CO₂ capture option:

CaCO₃ + sand + high heat → Kiln → alkaline cement kiln dust (CKD) → pH>12 → e.g., Ca(OH)₂ + 2CO₂ → Ca²⁺ + 2HCO₃⁻ → H₂O + CaCO₃ + CO₂ → Na,K,Mg Carbonates

CO₂ and Kiln Dust Mitigation in Cement Manufacture

Aqueous CO₂ + CKD contactor

<--CaCO₃ recycle -and/or- sequestration as CaCO₃
Features:

- Helps mitigate both CO$_2$ and CKD, esp legacy stockpiles of CKD
- Potential co-benefits
  - Recycle of waste Ca as CaCO$_3$
  - Can include air CO$_2$ capture
  - Selective precipitation of other useful compounds e.g. K, Mg, and Na carbonates, sulfates, etc.
  - Avoid landfilling and/or reclamation of landfills
- Retrofittable to existing plants
- Should be relatively low cost, <$3/tonne CO$_2$
  - Compared to >$25/tonne using CCS
  - Might profitable now without carbon credit/tax
Issues:

- Only relevant when/where/if CKD is available
  - Not applicable if CKD recycled in kiln
  - Not relevant if other uses of CKD outweigh CO$_2$ emissions reduction

- Will consume water via gas or air contacting and/or solar or waste heat evaporation.

- Might generate waste solutions; waste permitting issues

- Will require capital expenditure and space

- More R&D needed to determine cost effectiveness
CKD flue gas scrubber has been demonstrated

http://www.netl.doe.gov/technologies/coalpower/cctc/cctdp/bibliography/demonstration/ia/bia_cemkiln.html
DOE conclusions:

CKD can be used successfully as the sole reagent for removing SO₂ from cement kiln flue gas, with removal efficiencies of 90 percent or greater.

Removal efficiencies for HCl and VOCs were approximately 98 percent and 70 percent, respectively.

Particulate emissions were low, in the range of 0.005 to 0.007 grains/standard cubic foot.

The treated CKD sorbent can be recycled to the kiln after its potassium content has been reduced in the scrubber, thereby avoiding the need for landfilling.

The process can yield fertilizer-grade K₂SO₄, a saleable by-product.

Waste heat in the flue gas can provide the energy required for evaporation and crystallization in the by-product recovery operation.

**Estimated net after-tax profit = $2.6M/yr**
**Payout of investment in 3.2 years**
However, proposals to the Portland Cement Assoc. and to Cal’s Air Resources Board were not funded:

2007 ICAT Proposal:

**Demonstration of CO₂, SOₓ, NOₓ, and CKD Mitigation at a California Cement Plant**

Applicant:

Greg Rau, Ph.D.
Senior Researcher
Institute of Marine Sciences
University of California, Santa Cruz (off-campus)
L-640, bldg. 543, rm. 2070
Lawrence Livermore National Laboratory
7000 East Ave.
Livermore, CA 94550 USA
tel (925) 423-7990
fax (925) 423-0153
rau4@llnl.gov

Partner:

Envitech, Inc.
2924 Emerson Street - Suite 320
San Diego, CA 92106
POC: Andy Bartocci
Ph: (619) 223-9925
Fx: (619) 223-9338
abartocci@envtechinc.com
www.envtechinc.com

Figure 2. Schematic of demonstration set-up involving CKD solubilization, alkaline solution generation, alkaline stripping of acid flue gas in a scrubber, and precipitation of useable/storable/recyclable products. The system will be designed and built by Envitech, Inc.
Other Aqueous Chemistry-Based $CO_2$ Mitigation Ideas---->
Produced Water Re-injection with CO₂ Capture + Geologic Storage:

Primary separation:
- gases + CO₂
- solids
- flotation
- flocculation
- skimming
- settling

Secondary separation with CO₂ addition:
- CO₂ + H₂O + CO₃²⁻ → 2HCO₃⁻
- CO₂
- Limestone, waste carbonates
- Low-pressure, waste CO₂
- Produced Water + Dissolved Carbon Injection

- Water storage, isolation from air

Oil + Water + Gas Lifting
Use of CO$_2$ as an oxidant in an Fe fuel cell:

$$\text{Fe}^0_{(s)} + \text{CO}_2(g) + \text{H}_2\text{O}_{(l)} \rightarrow \text{FeCO}_3(s) \downarrow + \text{H}_2(g) \uparrow + 61.2 \text{kJ}$$

**Schematic of Fe/CO2 Fuel Cell Battery Operation:**

- Scrap Iron input
- Used Anodes
- Scrap Iron Processing
  - Anode Formation
- Fe Waste
- Scrap Iron Processing
- Fe Anodes
- Waste gas
- H$_2$/gas collection and cleanup
- H$_2$ output
- Waste gas
- Voltage/Current Processing?
- Hi/Lo VAC output
- Fuel Cell Battery Array
- H$_2$O/CO$_2$ equilibration
  - H$_2$CO$_3$ formation
- Used electrolyte
- CO$_2$ recycle
- FeCO$_3$ Stripping
- FeCO$_3$ storage/output
- H$_2$O recycle
- Fe$^{++}$ output to ocean?
- H$_2$O input
- H$_2$O input
- CO$_2$ cleanup?
- CO$_2$ input
- Waste CO$_2$ input

**Figure 1**
### Fe/CO₂ Fuel Cell Requirements, Yields, Costs

<table>
<thead>
<tr>
<th>Mass in (tonnes):</th>
<th>Mass/energy out:</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Fe⁰ --&gt;</td>
<td>2.07 FeCO₃ --&gt;</td>
</tr>
<tr>
<td>0.79 CO₂ --&gt;</td>
<td>0.04 H₂ --&gt;</td>
</tr>
<tr>
<td>0.32 H₂O --&gt;</td>
<td>300 kWhₑ</td>
</tr>
</tbody>
</table>

**Cost per tonne Fe:**

<table>
<thead>
<tr>
<th>Cost</th>
<th>Fuel cell</th>
<th>Output value per tonne Fe:</th>
</tr>
</thead>
<tbody>
<tr>
<td>$100 Fe⁰</td>
<td>Fuel cell</td>
<td>$15 CO₂ avoid. (@$20/tonne)</td>
</tr>
<tr>
<td>$30 COM</td>
<td>Fuel cell</td>
<td>$60 H₂ ( @$1.50/kg H₂)</td>
</tr>
</tbody>
</table>

**Net cost** = ($130-$90)/0.79 = $50/tonne CO₂ mitigated?
Use renewable DC electricity to allow:

- Production of air CO$_2$ absorbing solutions while generating “green” hydrogen.
  - 22 tonnes CO$_2$ absorbed per tonne H$_2$ produced
  - thus, novel production of carbon-negative hydrogen.
- Addition of alkalinity to seawater neutralizes or offsets ocean acidity.

Electrochemical production of alkalinity for CO$_2$ mitigation and carbon-negative H$_2$ production

Air CO$_2$ → 0.5O$_2$ and/or other gases

0.5O$_2$ → Ca(HCO$_3$)$_2$(aq)

H$_2$O → 2H$^+$ (anode)

2OH$^-$ (cathode) → 2H$_2$O + 2e$^-$

CaCO$_3$(s) → Ca(HCO$_3$)$_2$(aq)

DC Electricity Source

saline solution level
Experimental results -
Alkalinity generated, air $\text{CO}_2$ absorbed

Lots of assumptions, but -

Electricity Source
Net $\$/tonne CO$_2$ avoided
Average electricity 2015

- PV 241
- NGCC electricity 165
- Wind 40-80

Solution pH

![Graph showing pH over elapsed time with two different conditions: -CaCO$_3$ and +CaCO$_3$.]
For Example: Ocean-based, carbon-negative wind hydrogen production.
Conclusions:

- Continued reliance on fossil fuel energy in a carbon-constrained world requires that multiple, cost-effective and safe CO₂ sequestration technologies be quickly found and deployed.

- For point source mitigation, relying solely on the capture and storage of CO₂ in molecular form (CCS) is unnecessary and unwise because inherent capture/separation costs, and local availability of safe, secure storage may delay/limit application.

- A variety of chemistry-based sequestration approaches are available and/or may emerge; these need to be pursued - the cement industry is a prime example.

- Let’s get going! Partners and funding sought.