
Low-cost Options for CO₂ Mitigation in Electricity, Oil, and Cement Production

Greg H. Rau

***Institute of Marine Sciences
University of California, Santa Cruz
and***

***Energy and Environment Directorate
Lawrence Livermore National Laboratory***

rau4@llnl.gov

Outline:

- ❑ Why post-combustion CO₂ sequestration is needed.
- ❑ CO₂ capture/storage options, and R&D at LLNL.
- ❑ Chemistry-based approaches for CO₂ removal from waste gas streams (and air).

Conclusions:

- ❑ CO₂ sequestration should not be ignored in California's strategy for meeting its CO₂ mitigation goals.
- ❑ Continued reliance on fossil fuels in a carbon-constrained world (and State) will require that CO₂ sequestration technologies be found and deployed in the coming decades.
- ❑ Cost-effective and safe chemical CO₂ sequestration options are available, but need to be further researched and evaluated.
- ❑ Partners and funding for R&D are needed.

Why CO₂ Mitigation?

It's Not Just Because of Climate Impacts!

Adding CO₂ to the Atmosphere adds CO₂ to the ocean
= Ocean Acidification:

Air-to-sea diffusion of CO₂ into seawater:



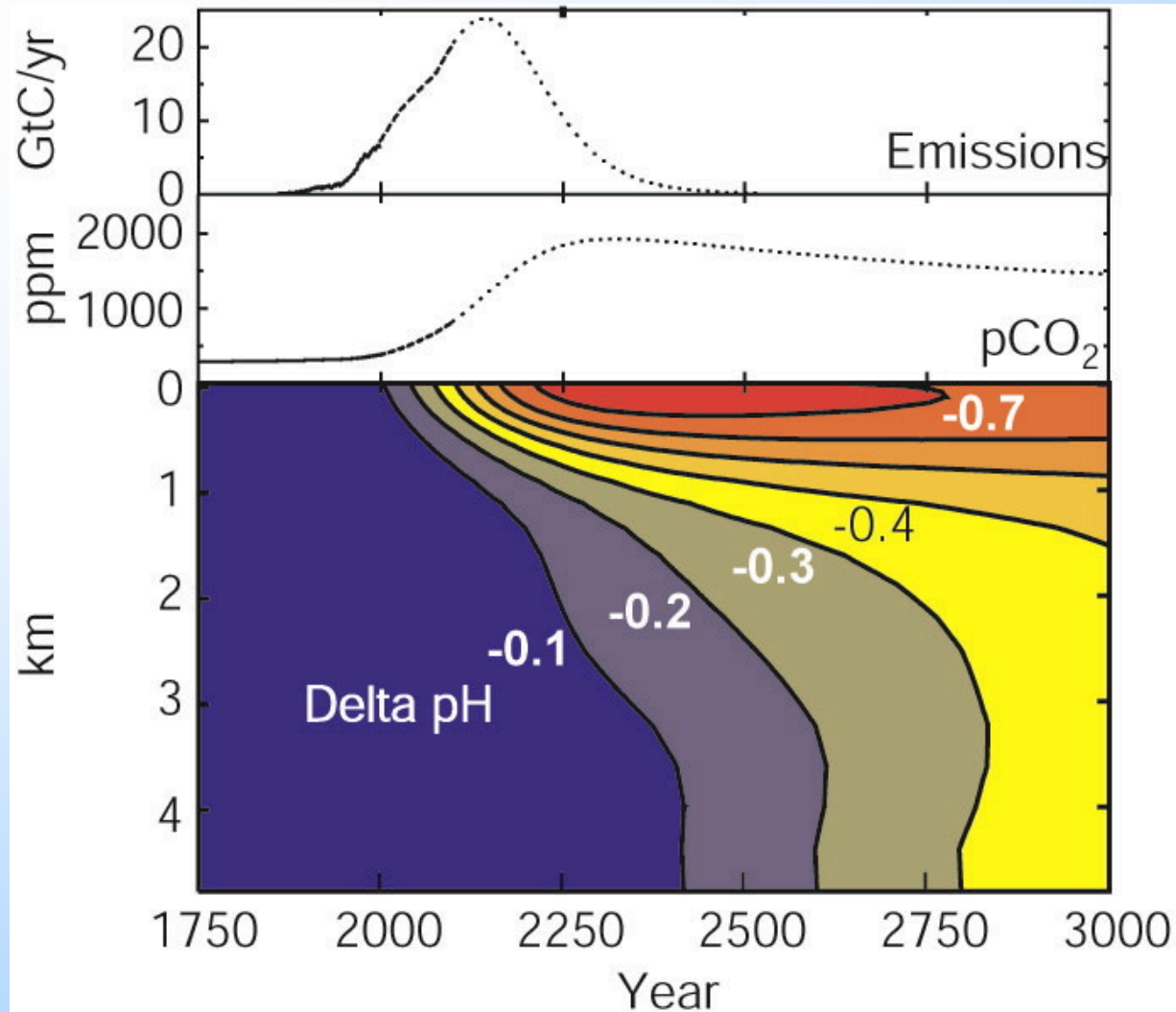
Fate of CO₂ added: (+ 9 %) (+151 %) (– 60%)

ocean relationships: [CO₂]↑ [H⁺]↑ pH↓ [CO₃²⁻]↓

➔ For each mole of CO₂ added ~0.9 mole H⁺ is produced.

***Therefore, the annual net ocean uptake of 2Gt C
(=7.3Gt CO₂) produces about 0.15Gt of H⁺.***

CO₂ Emissions Impact on Ocean pH:



(Caldeira and Wickett, 2003, *Nature* 425:365)

Consequences of Ocean pH Decrease:

Reduced calcification of marine plankton in response to increased atmospheric CO₂

Ulf Riebesell*, Ingrid Zondervan*, Björn Rost*, Philippe D. Tortell†, Richard E. Zeebe*‡ & François M. M. Morel†

Nature 407: 364-

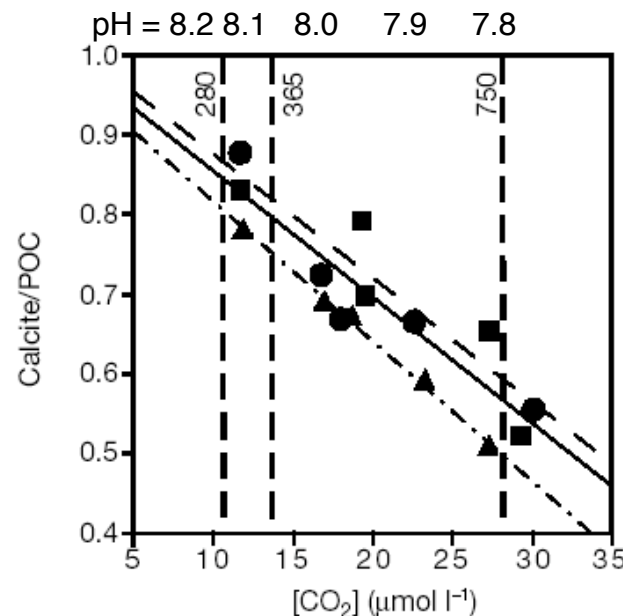


Figure 2 Ratio of calcification to POC production (calcite/POC) of *Emiliana huxleyi* as a function of CO₂ concentration, [CO₂]. Cells were incubated at photon flux densities of 30, 80 and 150 μmol m⁻² s⁻¹ (denoted by circles, squares and triangles and corresponding solid, dashed, dash-dotted regression lines, respectively). Bars denote ± 1 s.d. (*n* = 3); lines represent linear regressions. Vertical lines indicate *p*CO₂ values of 280, 365 and 750 p.p.m.v.

State Response to CO₂ Threat:

AB 32:

AND OCEAN ACIDIFICATION

DIVISION 25.5. CALIFORNIA GLOBAL WARMING SOLUTIONS
ACT OF 2006

PART 1. GENERAL PROVISIONS

CHAPTER 1. TITLE OF DIVISION

38500. This division shall be known, and may be cited, as the
California Global Warming Solutions Act of 2006.

Other Legislation/Executive Orders:

AB 1493

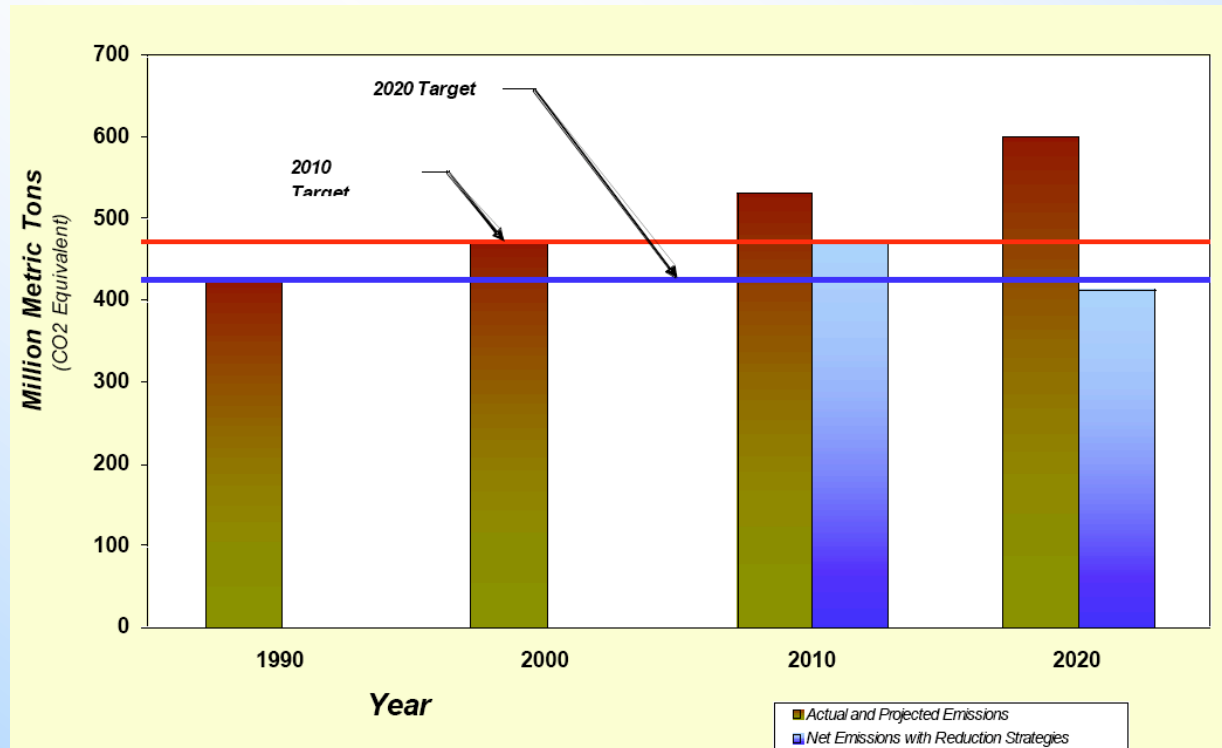
S-3-05

AB 1368

AB 1925

AB 32 Goal:

“...require the state board [CARB] to adopt a statewide greenhouse gas emissions limit equivalent to the statewide greenhouse gas emissions levels in 1990 to be achieved by 2020...”



(CAT, 2006)

---> 174 MMTCO₂e/yr (29%) reduction over BAU by 2020

How to Achieve Goal?

Center for Clean Air Policy Report, Jan. 2006:

■ *California can achieve 86% of its 2020 emissions reduction target by applying known technologies/methods that on average will cost \$5.77/tonne of CO₂ avoided.*

➤ *Does not require participation by electricity production and oil refining.*

➤ *No mention of CO₂ sequestration.*

■ *The total emissions target can be achieved at no cost to consumers if additional emissions reduction cost no more than \$123/tonne CO₂ avoided.*

How to Achieve Goal - Part 2

Climate Action Team Report - March, 2006:

California can meet or exceed its 2020 emissions reduction target by applying known technologies/methods principally to transportation, fossil energy, renewable energy, and forest/ag sectors.

- *Includes mitigation of non-CO₂ GHG's*
- *Anticipated low net cost, and positive effects on economy*
- *No mention of CO₂ sequestration.*

How to Stabilize Atmospheric CO₂

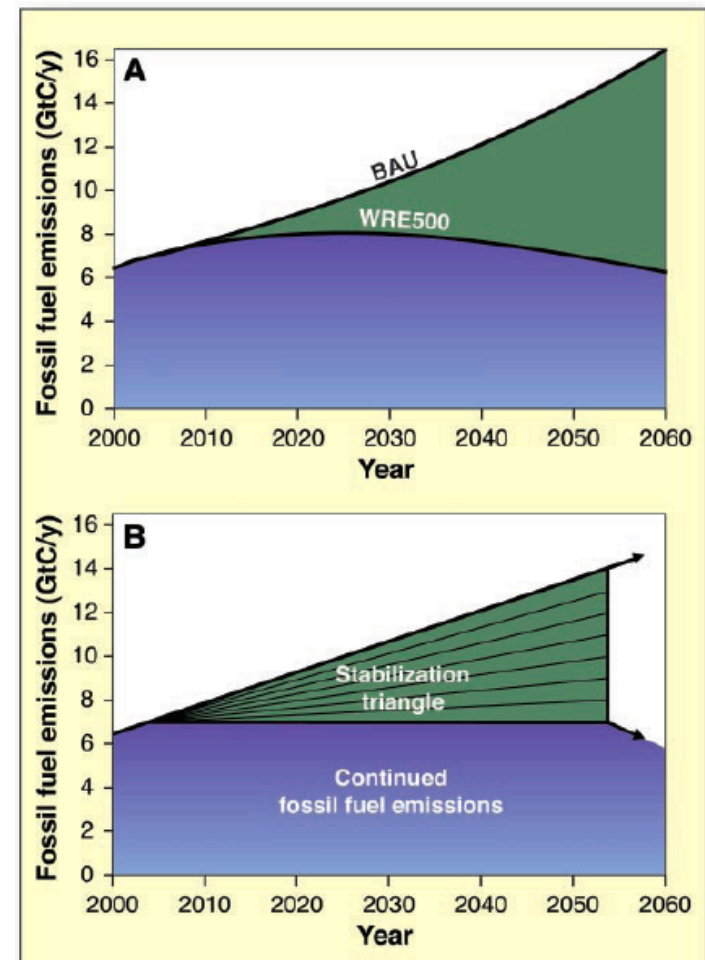
- A Less Rosy View

Pacala and Socolow (2004, Science 305:968-):

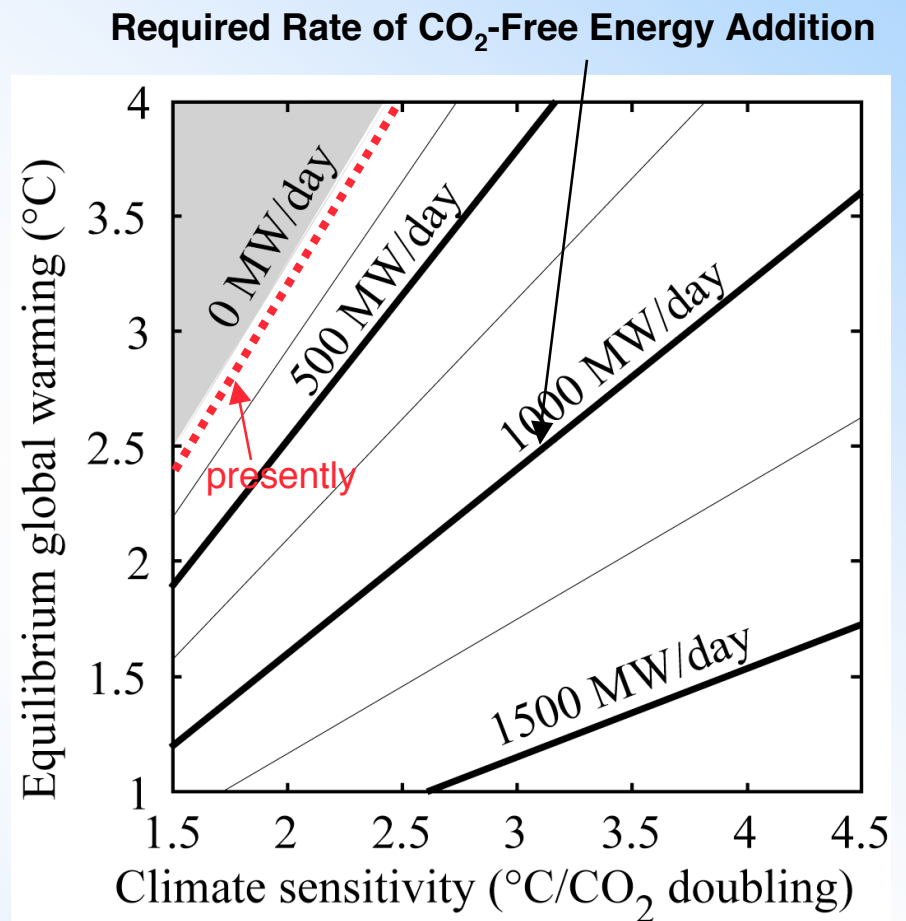
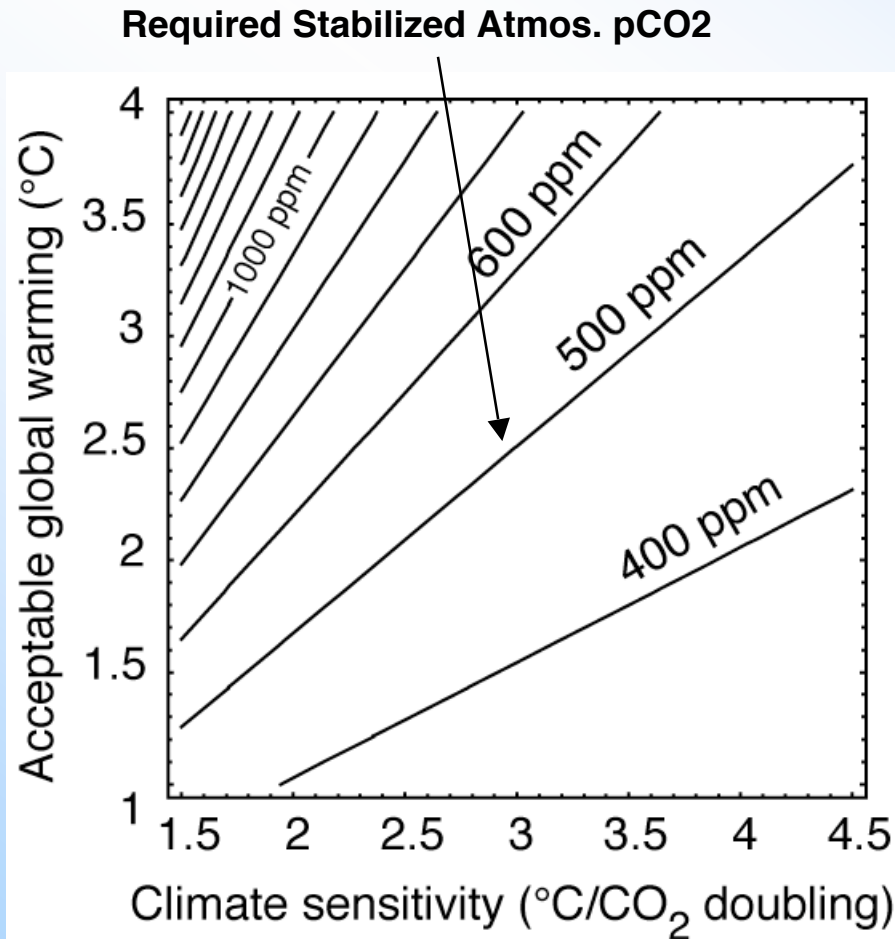
To stabilize atmospheric CO₂ at 500 ppm by 2054 -

■ *Emissions must be reduced by 1/3 over the next fifty years.*

■ *Draconian application of existing/known technologies is required, including CO₂ sequestration, especially in the context of hydrogen and coal-to-synfuels production.*



50-yr Projected $p\text{CO}_2$ and CO_2 -Free Energy Requirements for Various Climate Sensitivities and Global Warmings:



(Caldeira et al., 2003, *Science* **299**: 2052-)

To add 1 GW_t of CO₂ Free power capacity each day:

- Biomass @ 5 W / m²
 - 200 km² land area suitable for agriculture each day
- Wind @ 30 W_e / m²
 - 20 km² suitably windy land area each day (~500 wind turbines per day) [+ storage and distribution]
- Solar @ 66 W_e / m²
 - 5 km² of solar cells on suitably sunny land each day [+ storage and distribution]
- Fission
 - One 300 MW_e fission plant coming on line each day [assuming energy can be used as electricity! 1 GW if needed for heating, etc.]
- Solutions must be applicable to developing countries, where most of the increase in emissions is expected to occur
- **Thus, fossil fuel use WITH CO₂ sequestration appears essential.**



The Role of CO₂ Sequestration in California?

CO₂ sequestration should be include in California's CO₂ mitigation portfolio because:

- ☐ It would reduce the need for efficiency, renewables, and forest/ag management to satisfy all CO₂ reductions - sequestration can fill in mitigation shortfall.
- ☐ Sequestration will likely be needed in longer term, especially in a fossil-energy-based hydrogen/synfuels economy.
- ☐ Sequestration may prove to be more cost-effective than other available CO₂ mitigation technologies.

CO₂ Capture/Sequestration Options:

☐ Land-Based

- Abiotic molecular CO₂ capture and purification with underground (geologic) storage
- Enhanced biological uptake/storage -
managed forests, crops, microbes, soils, etc
- Carbonation/mineralization reactions

☐ Ocean-Based

- Abiotic CO₂ capture plus direct CO₂ injection
- Enhanced bio uptake/storage
e.g., Fe, nitrate, etc fertilization

☐ Alternatives...

Activities in LLNL's Energy & Environment Directorate:

Four major programs:

- CAMS (Accelerator Mass Spectrometry)
- NARAC (Atmospheric Release)
- Nuclear Science & Engineering
- Earth System Science & Engineering

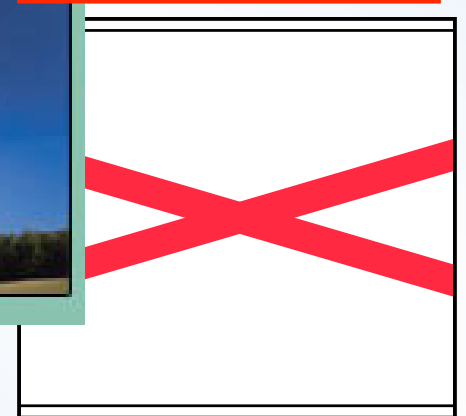
ESSE comprises for program elements

- Carbon management & fossil energy
- Water & environment (incl. energy-water nexus)
- Climate change prediction
- Energy technology & analysis

Combination of basic and applied science

- Simulation and experimentation
- Field programs and verification
- Funded by DOE and industry

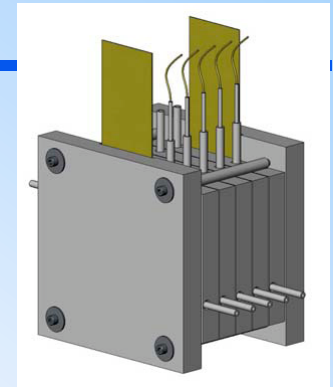
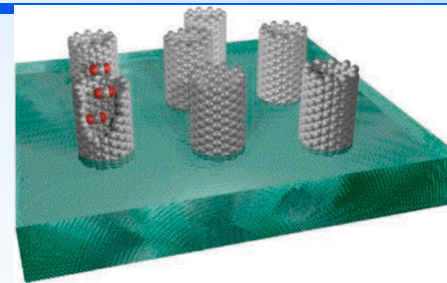
Service to government institutions and decision making process



Carbon Management Program Foci:

Novel CO₂ Capture

- Advanced membranes
- Accelerated Limestone Weathering
- Desalination and CO₂ Separation
- Direct Carbon Fuel Cell



CO₂ storage in geological formations

- Simulation (and experimentation)
 - Geomechanical effects
 - Reactive chemistry (e.g., groundwater)
- CO₂ Monitoring and verification (M&V)
 - Geophysical Integration
 - Source term Characterization
 - Operational protocols
- Risk characterization & assessment
 - Site characterization and assessment
 - Operational protocols
 - Hazard definition and management



Energy systems modeling

Fossil Energy (e.g., underground coal gasification)

Carbon Management Partners in CA, US, and World-Wide

California

- Charter member of WestCarb (CEC)
- CA companies and projects (e.g. BP, CES)
- Testified to assembly & senate



US programs

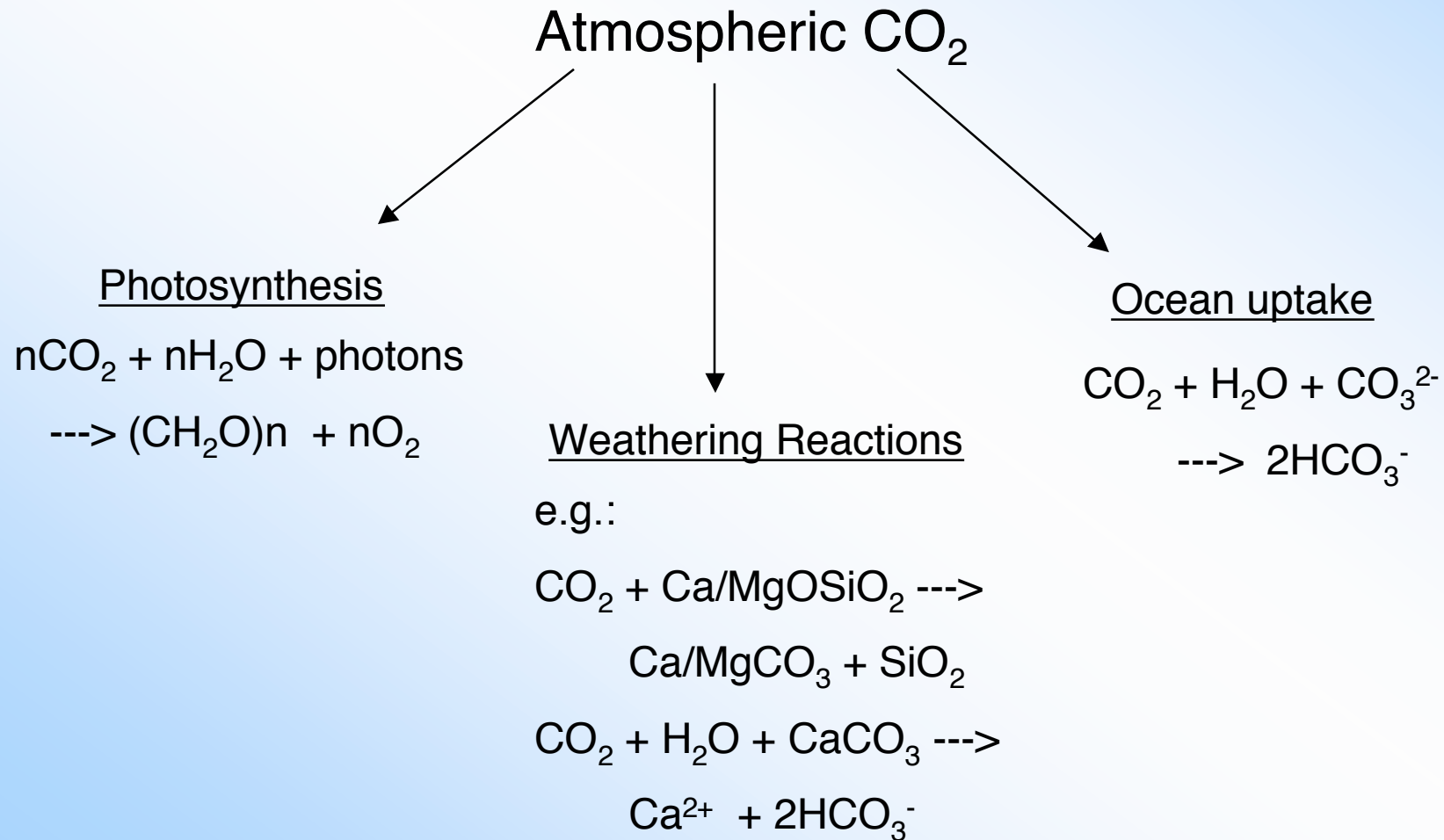
- 3 DOE Regional partnerships (including Westcarb)
- Fundamental Research (e.g., ZERT)
- Work with EPA on regulatory framework
- Partnerships with NGOs (NRDC, World Resource Institute, Great Plains Institute)
- Helping to develop international protocols for CCS

Internationally

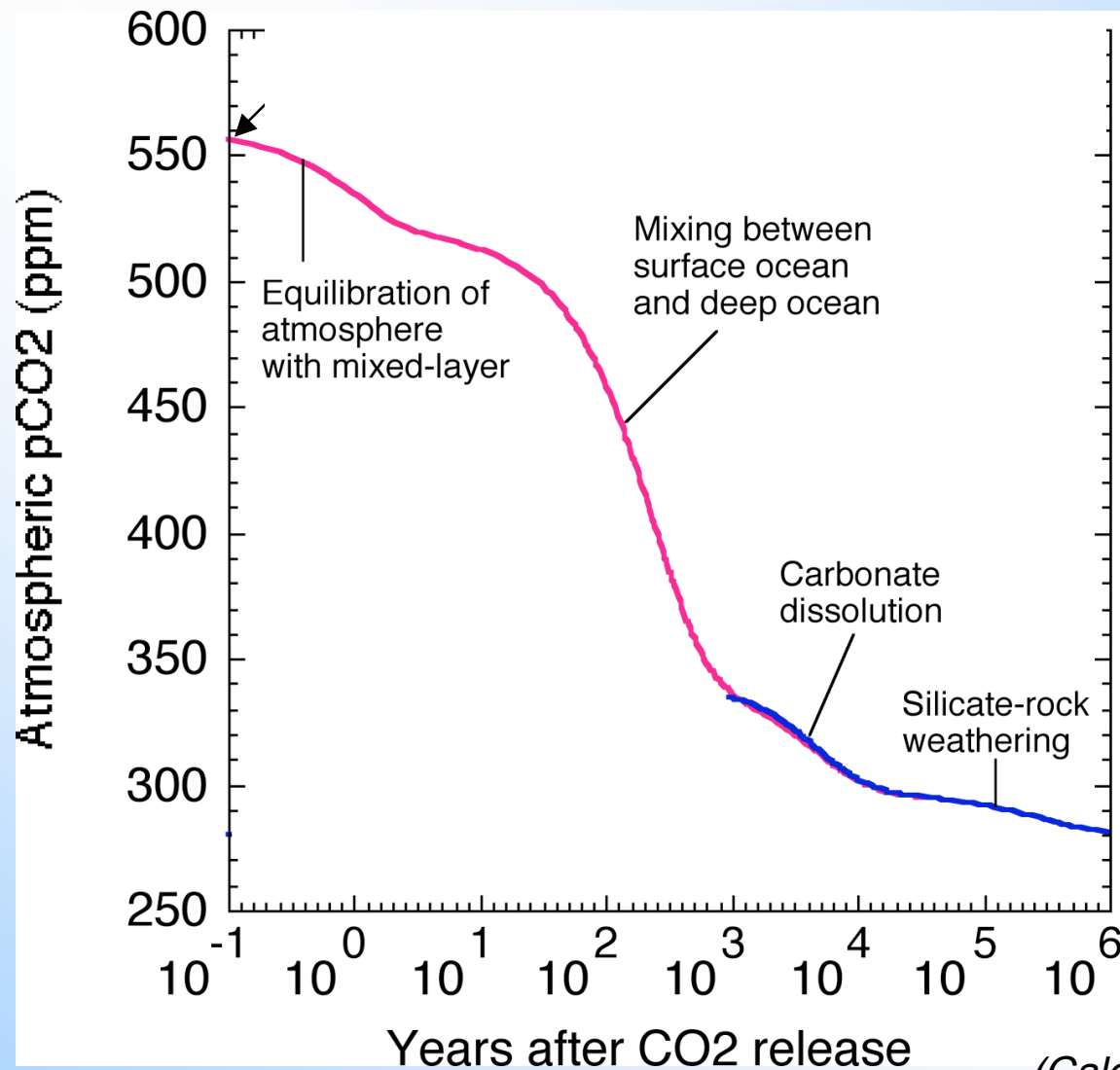
- Engaged on large projects (e.g., In Salah, Weyburn)
- Helping to develop international protocols for CCS through Carbon Sequestration Leadership Forum, industry
- Work with International Energy Agency on best practices
- Partnered with international companies, NGOs

Nature's Chemical CO₂ Capture and Storage:

Nature's own mechanisms:

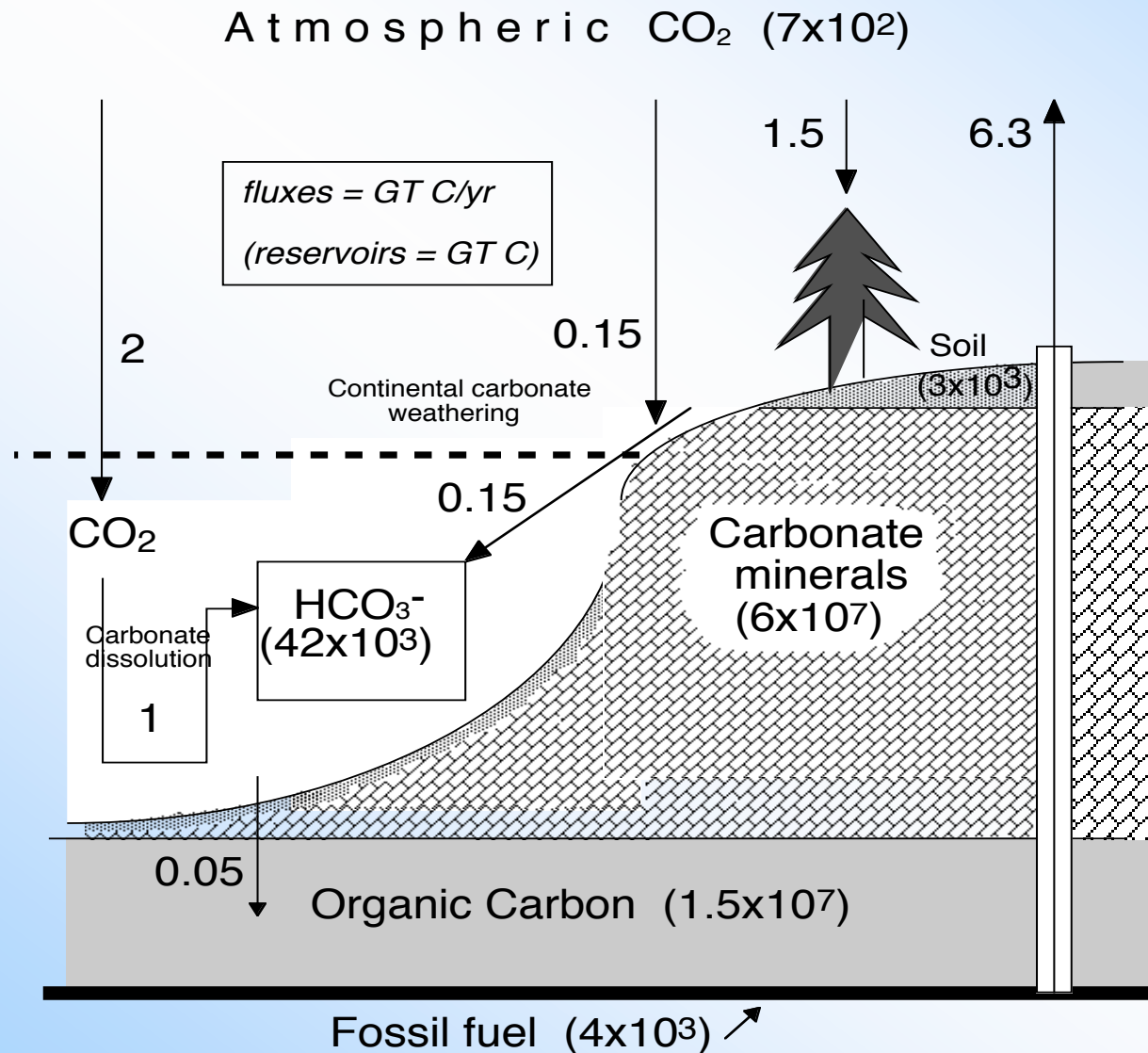


Natural CO₂ “Capture and Sequestration”:

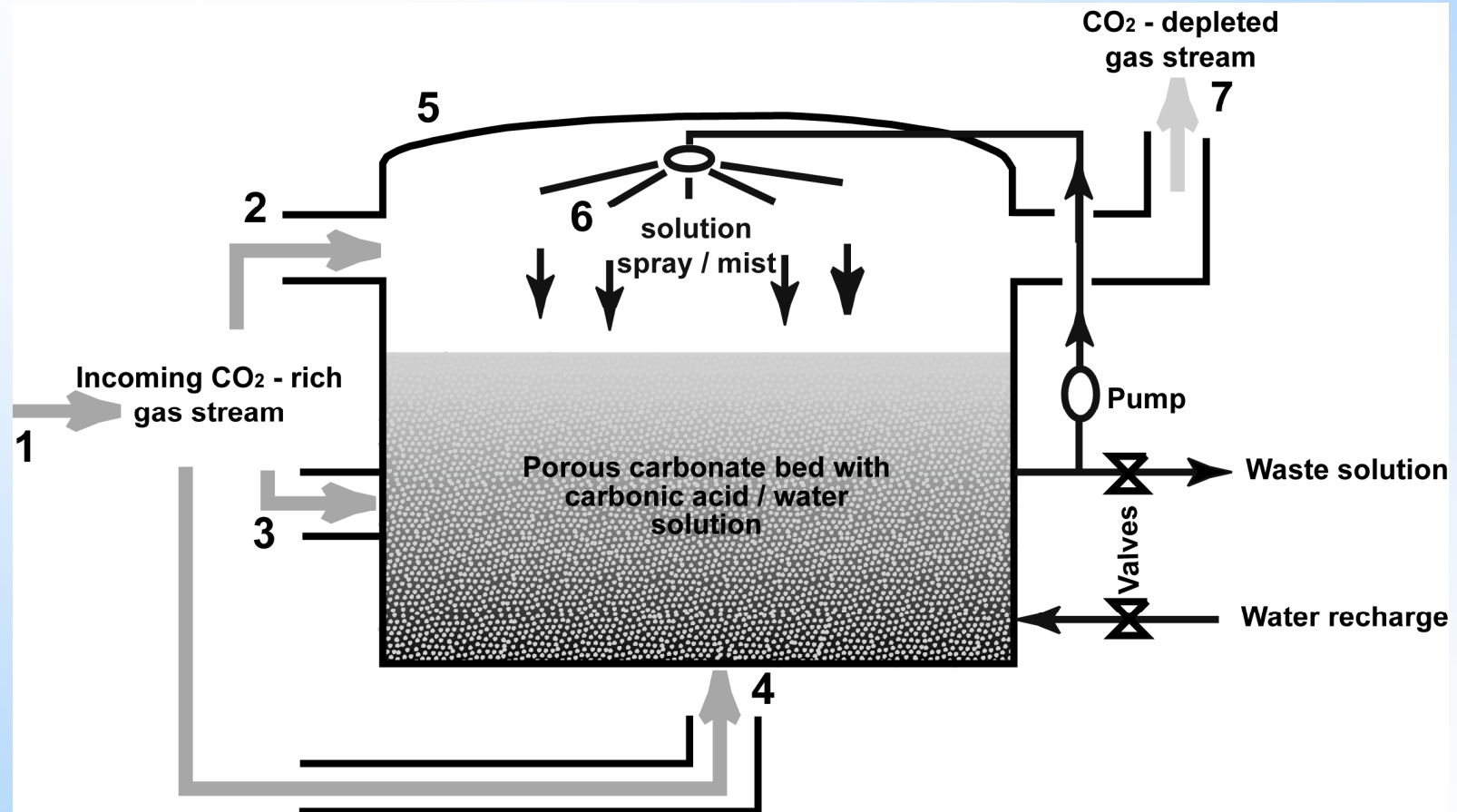


(Caldeira and Rau, 2000)

Carbonate Weathering in the Global Carbon Cycle:



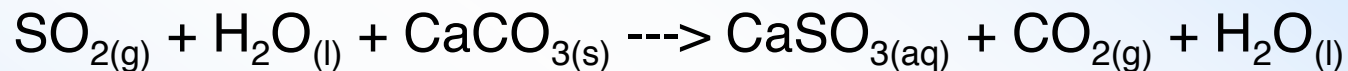
Accelerated Weathering of Limestone (AWL) Reactor:



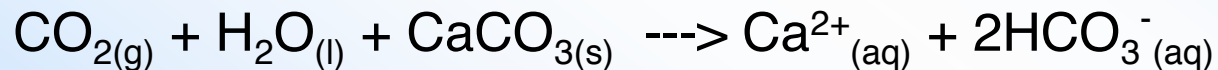
(Rau and Caldeira, 1999)

Analogies to Flue Gas Desulfurization:

FGD:

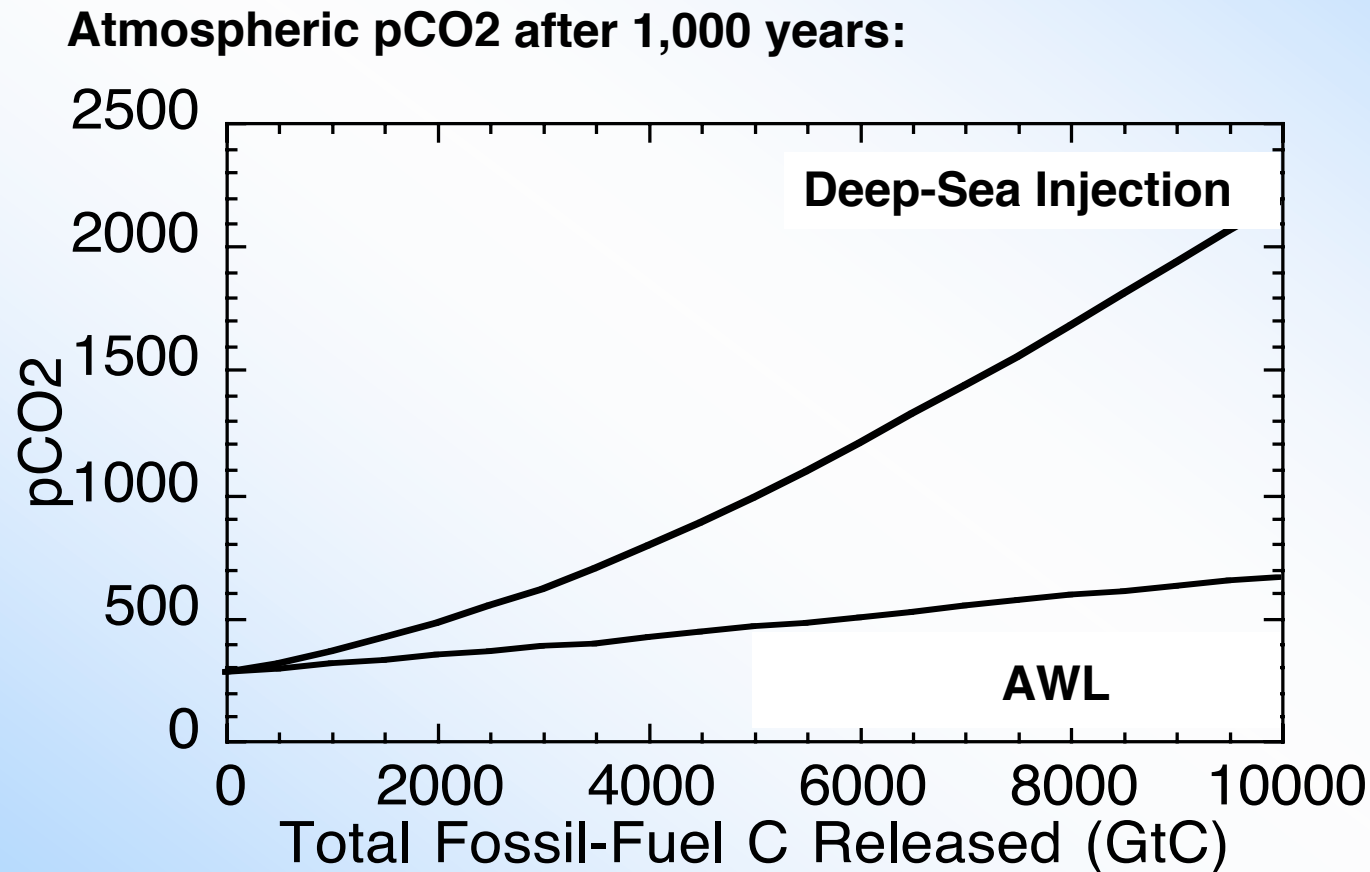


AWL:



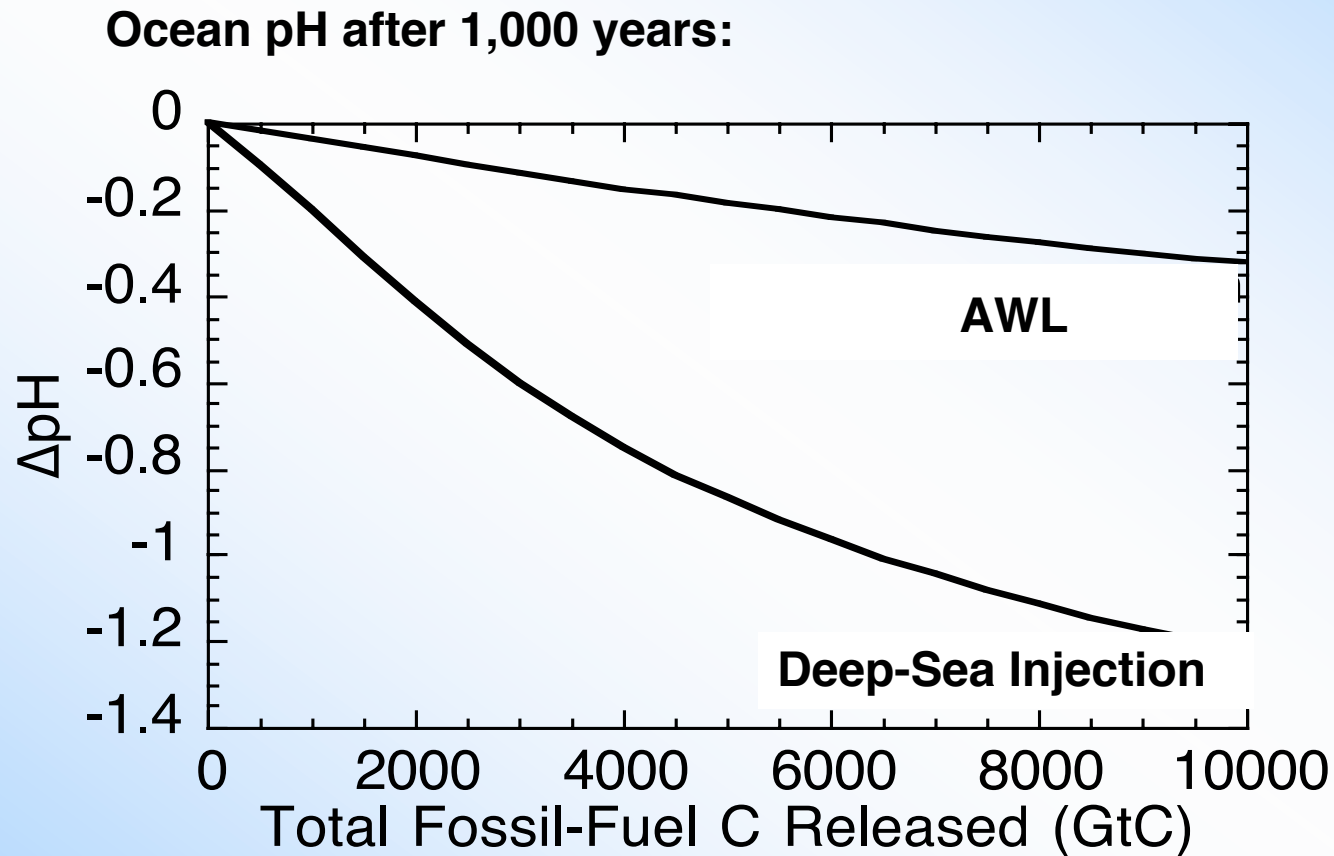
→ Gases captured via reaction with wet limestone (at ambient temperature and pressure), and converted to benign, storable/useable liquids or solids

Direct CO₂ Injection vs AWL - Effect on Atmospheric pCO₂:



(Caldeira and Rau, 2000)

Direct Injection vs AWL -Effect on Ocean pH:



(Caldeira and Rau, 2000)

AWL Economics:

- ❑ Estimated cost per tonne CO₂ sequestered, assuming coastal location:

- Limestone -

◆ 2.3 tonnes @ \$4/tonne =	\$ 9.20
◆ crushing from 10 cm to 1cm =	\$ 1.45
◆ transport 100 km by rail =	\$ 8.00

- Water -

◆ 10 ⁴ m ³ , pumped 2 vertical meters =	\$ 7.57
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- Capital and maintenance = \$ 2.50

TOTAL:

\$ 29/tonne CO₂

Compared to \$40-\$60/tonne for amine capture + geologic storage of CO₂ from a conventional power plant

Optimum AWL Economics:

Estimated cost per tonne CO₂ sequestered,
assuming coastal location:

➤ Limestone -

- ◆ 2.3 tonnes @ \$4/tonne = ~~\$ 9.20~~ | *use free, nearby*
- ◆ crushing from 10 cm to 1cm = ~~\$ 1.45~~ | *waste limestone*
- ◆ transport 100 km by rail = ~~\$ 8.00~~
- ◆ Water -
- ◆ 10⁴ m³, pumped 2 vertical meters = ~~\$ 7.57~~ | *use cooling water*

➤ Capital and maintenance = \$ 2.50

TOTAL:

<\$3/tonne CO₂

Advantages of AWL:

☐ Abundant and cheap reactants:

- Limestone - carbonates = $6 \times 10^7 \text{ Gt C}$, fossil fuels = $4 \times 10^3 \text{ Gt C}$;
H₂O - ocean = $1.4 \times 10^{18} \text{ m}^3$

☐ Relatively innocuous waste products:

- Primarily Ca²⁺ and HCO₃⁻ in solution; Avoids low pH inherent in passive or active CO₂ injection into ocean; benefits to marine biota

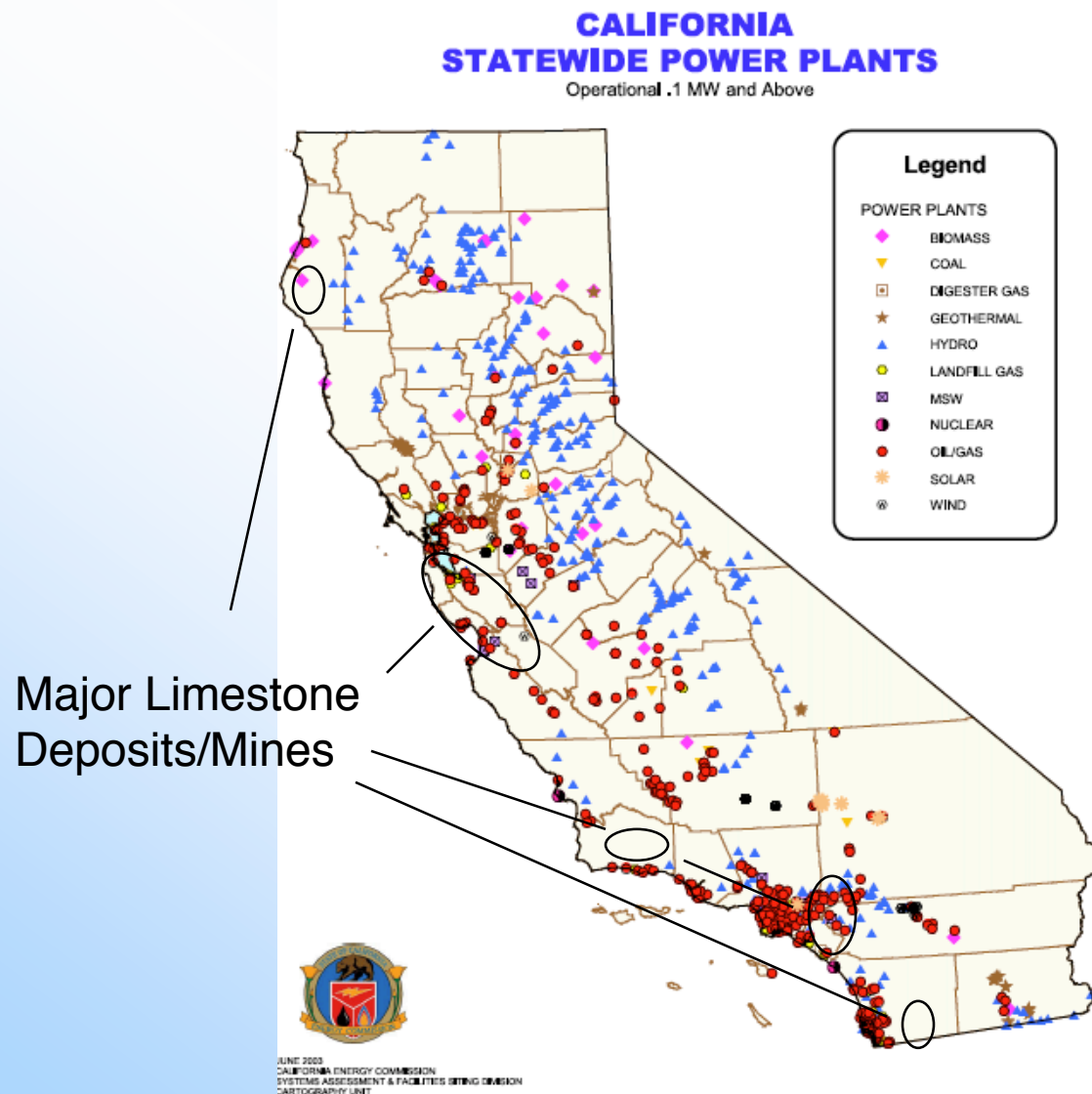
☐ Not energy- or technology-intensive:

- Does not require separate, costly CO₂ capture/concentration
- Can modify existing flue gas scrubbing technology
 - analogous to coal plant desulfurization

☐ Relatively inexpensive

- 10-20% US emissions mitigated at <\$30/tonne CO₂

Limestone Availability vs CA Coastal Power Plant Location:



Impacts/Issues Needing Further Research:

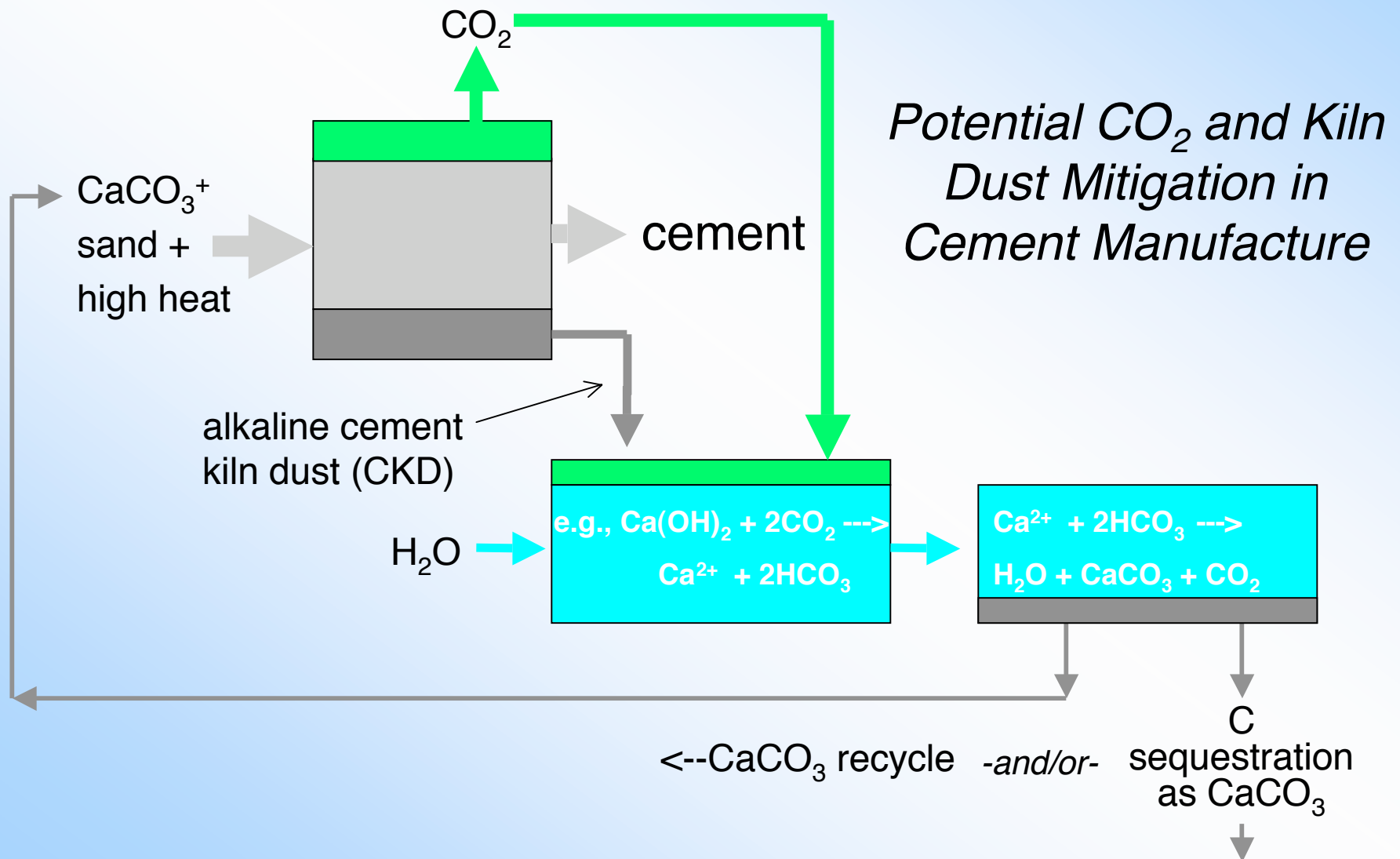
- ❑ Local availability of limestone and water limits application
 - could be offset by piping CO₂ to favorable AWL sites
 - use inland saline aquifer or water with oil?
- ❑ Marine biological impacts -
 - net beneficial?
 - trace contaminants from flue gas or limestone?
- ❑ Environmental, transportation, and economic impacts due to increased limestone mining/transport.
- ❑ Regional, national, and global assessments and R&D needed. Proposal submitted to CEC PIER program.

CO₂ Mitigation In Cement Manufacture:

CCAP Report 2005: CA Cement Manufacture -

- ❑ Current state emissions ≈ 10.5 MMT CO₂/yr
- ❑ Cumulative emissions by 2020 = 260 MMTCO₂
- ❑ Can be reduced by 47 MMTCO₂ by 2020 at a cost <\$10/tonne CO₂ via:
 - Limestone or flyash + cement blends
 - Alternative fuels
- ❑ But there is industry/public resistance to these options
 - Alternatives needed

Combined CO₂ and Kiln Dust Mitigation:



Features/Issues:

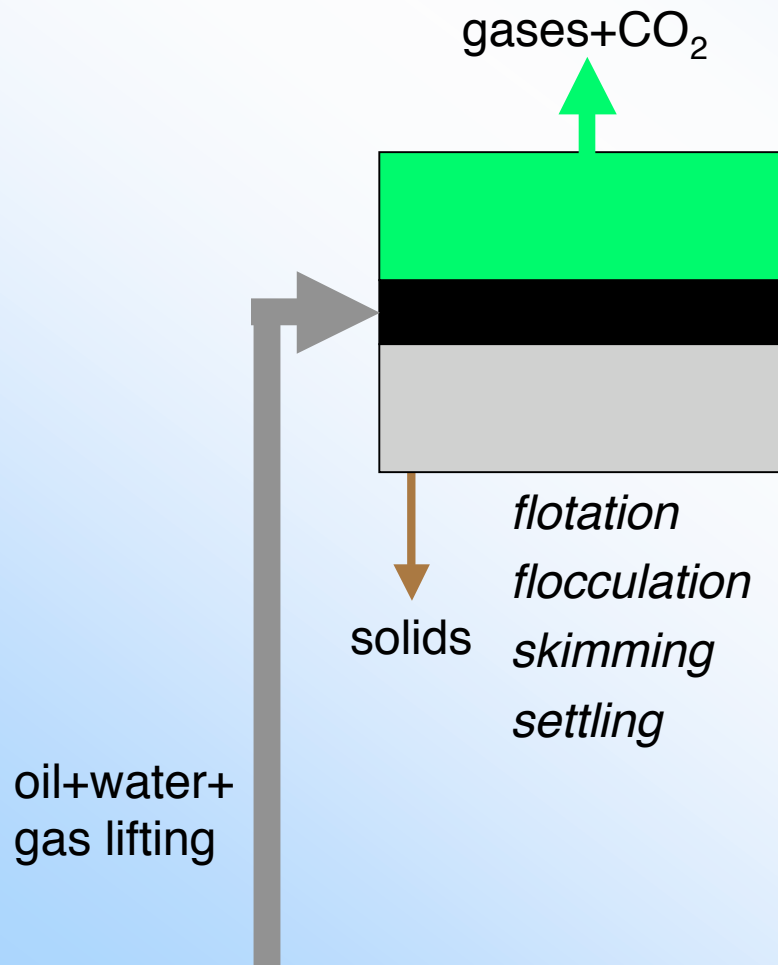
- Helps mitigate both CO₂ and CKD
- Potential co-benefits
 - Recycle of waste Ca as CaCO₃
 - Selective precipitation of other useful compounds e.g. K, Mg, and Na carbonates
- Should be very low cost, maybe <\$1/tonne CO₂
- Further evaluation and testing needed. Proposal submitted to Portland Cement Association.

CO₂ Sequestration Using Water Co-Produced With Oil:

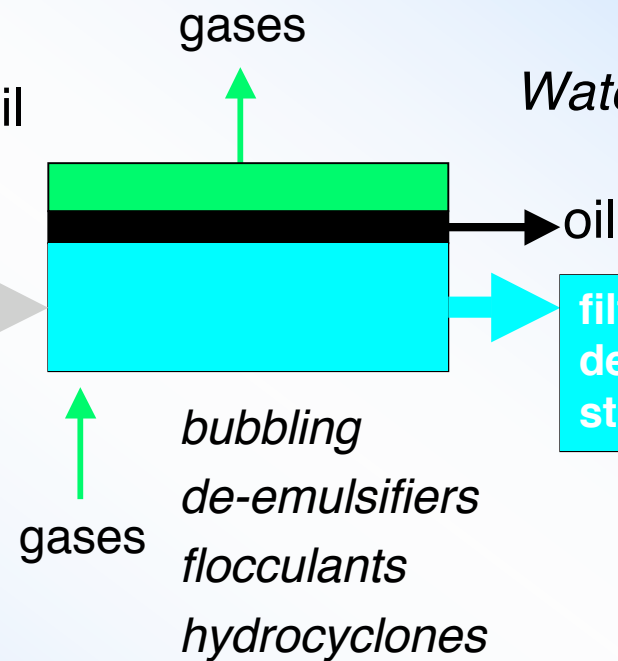
- On average 10 barrels of water are brought to the surface with every barrel of oil produced.
- CA produces 650 Mb oil/yr, therefore 2.7×10^{11} gals (?) water produced; Majority of water is injected back into ground.
- These waters are on average alkaline and undersaturated with respect to typical CO₂ waste streams (based on analysis of Texas produced waters).
- Therefore why not equilibrate these waters with waste CO₂ (+-limestone) to effect very low cost CO₂ capture and safe geologic storage? Co-benefits:
 - reduced scaling and microbial fouling
 - enhanced oil recovery and oil/water separation?

Typical Produced Water Scheme:

Primary separation:



Secondary separation:

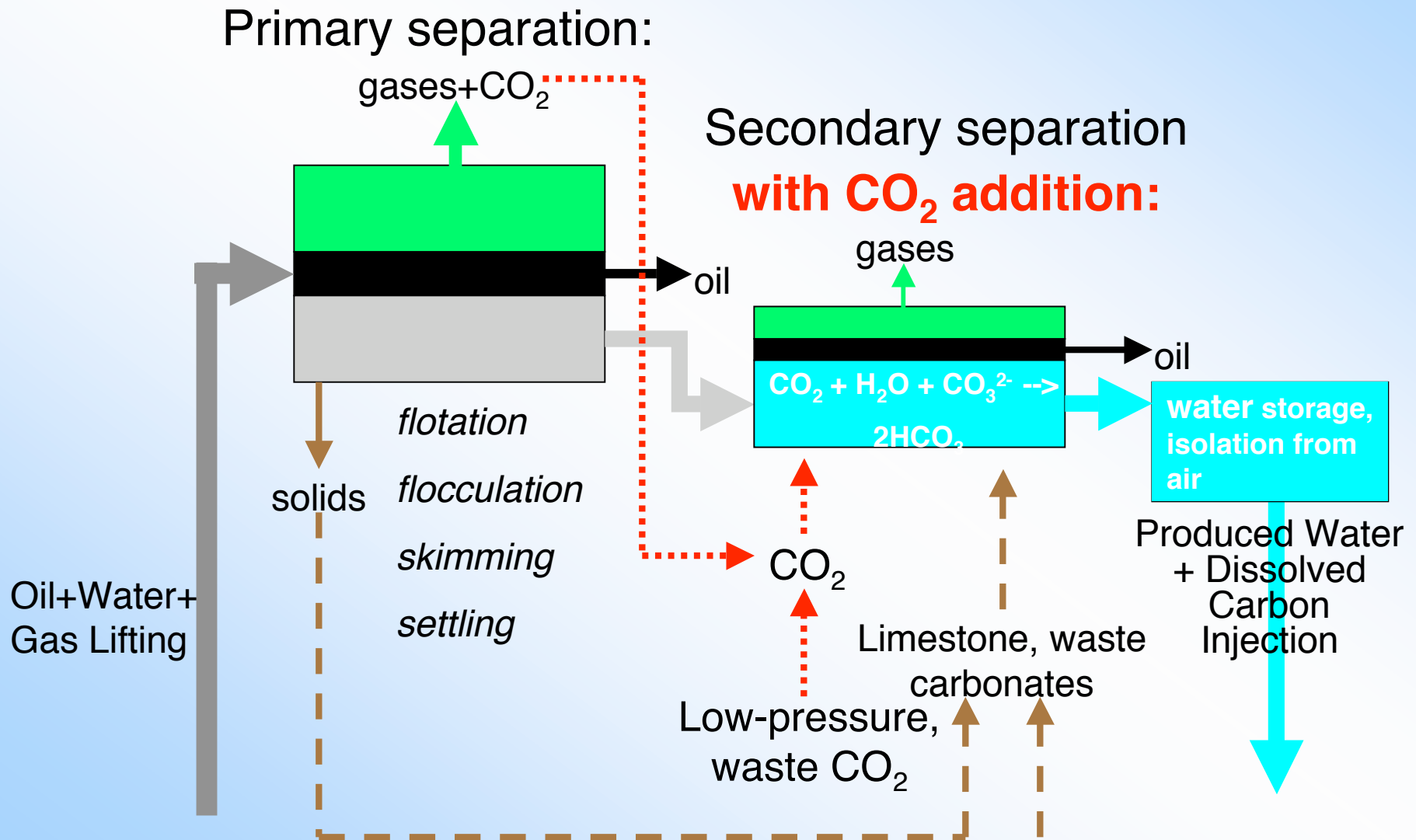


Water finishing:

filtration,
degassing,
storage

produced
water
injection

Produce Water with CO₂ Capture +Geologic Storage:

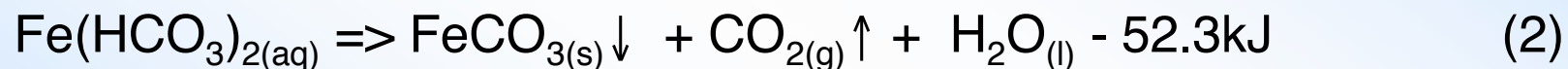


Another Idea: Iron/CO₂ Fuel Cells?

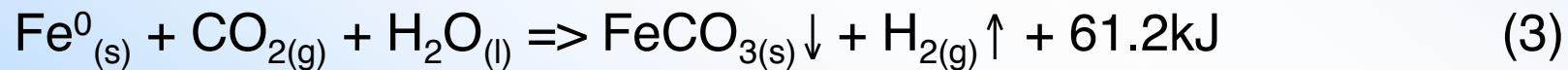
From corrosion science:



$$\Delta G = -2.2\text{kJ @ } 25^\circ\text{C}$$



Net reaction:

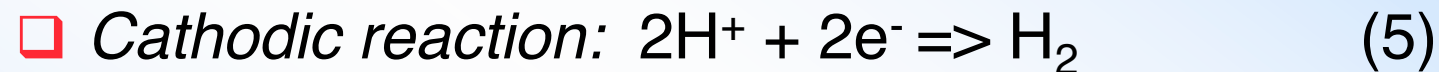
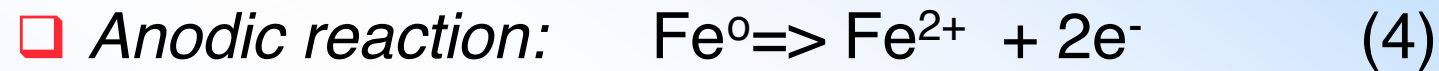


$$\Delta G = -35.2\text{kJ @ } 25^\circ\text{C}$$

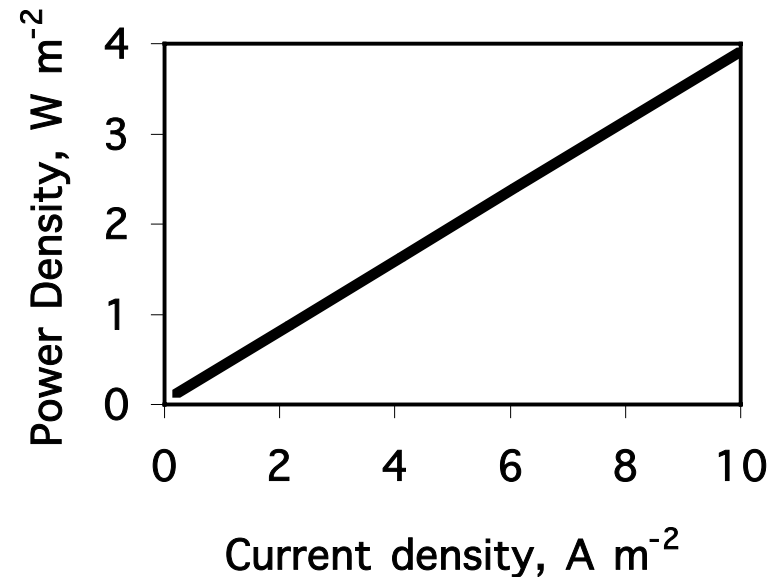
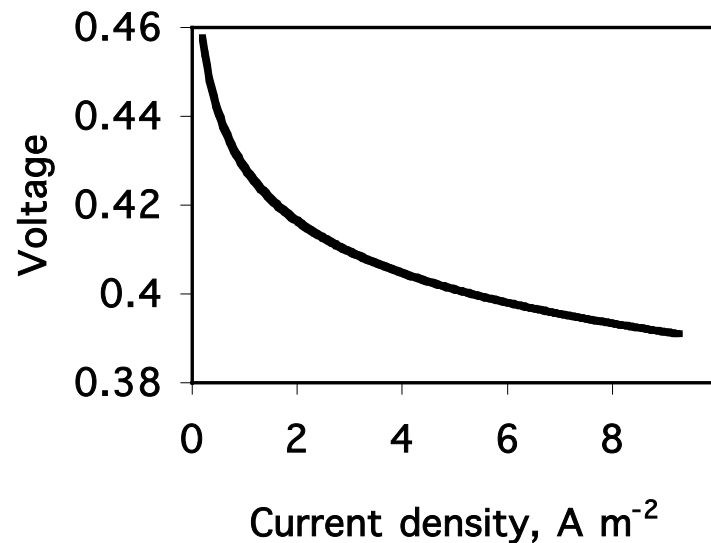
Thus, at ambient temperature and pressure:

- ☐ CO₂ converted to a dissolved bicarbonate or solid carbonate
- ☐ hydrogen gas is produced
- ☐ electricity is produced ----->

Electricity Generation - an Fe/CO₂ Galvanic Cell:



e.g., from Hasenberg (1988):



Possible Fe/CO₂ Fuel Cell Design:

Example of Fe/CO₂ Fuel Cell:

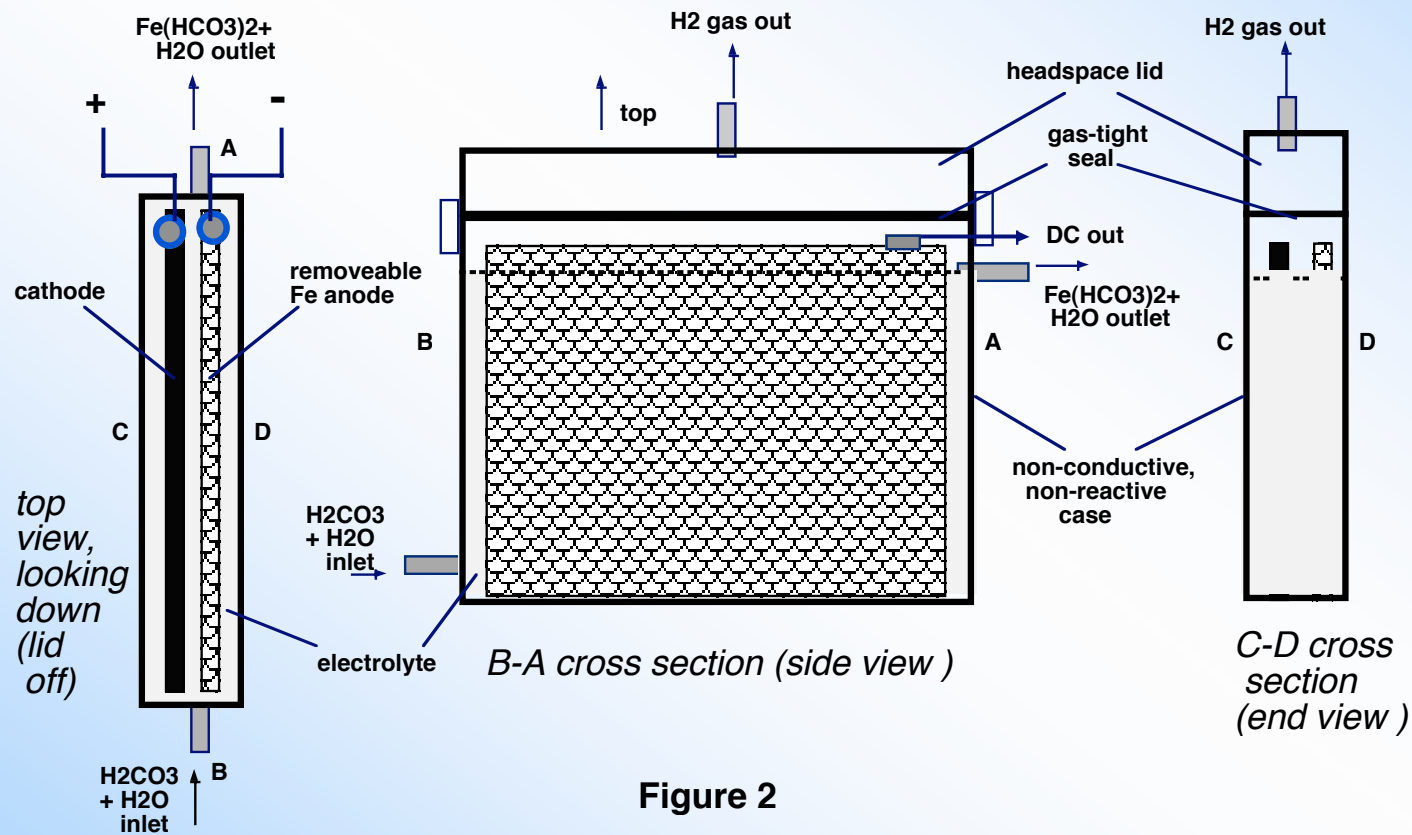


Figure 2

Large-Scale Fe/CO₂ Fuel Cell Operation:

G.H. Rau
Aug 11'03

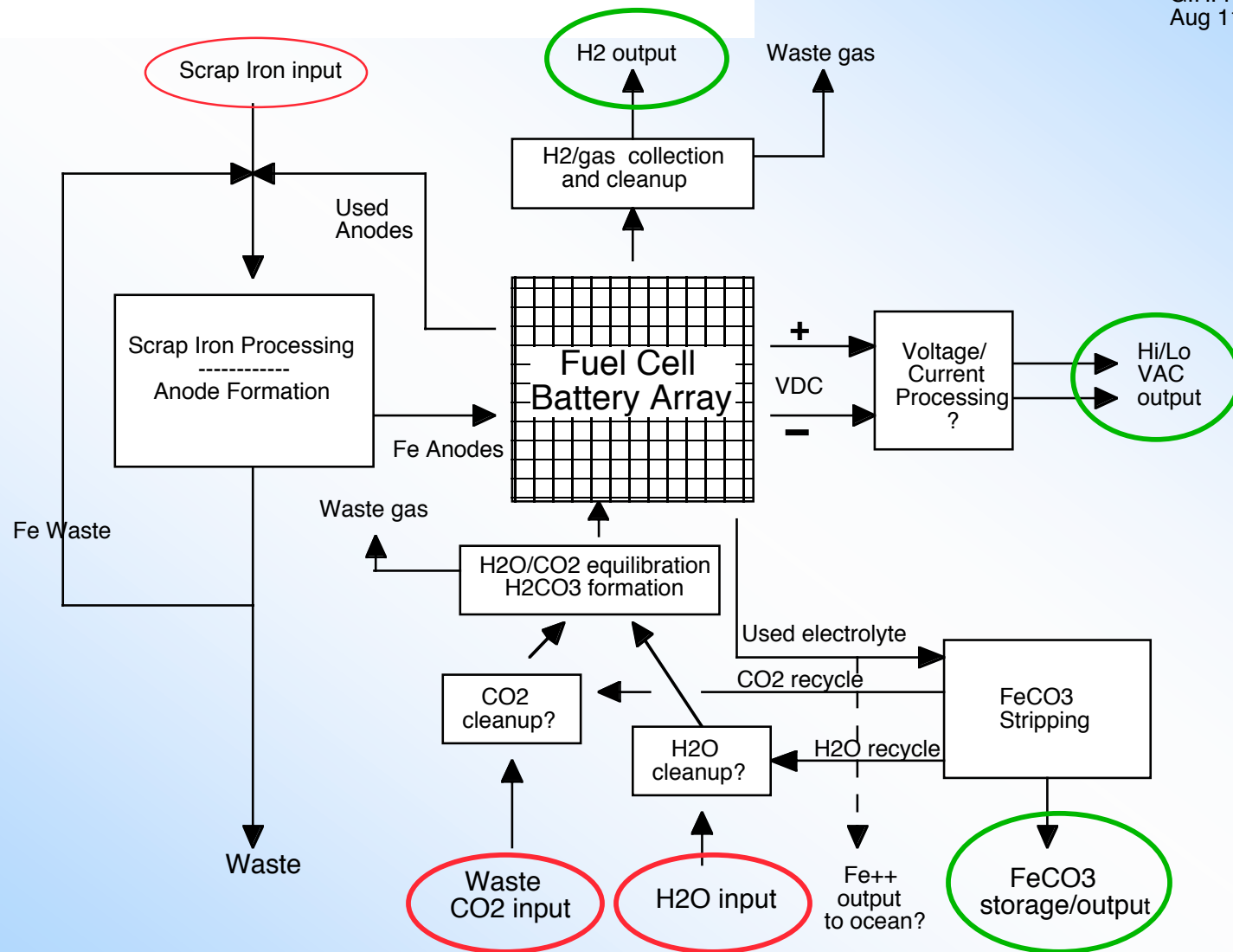


Figure 1

Fe/CO₂ Fuel Cell Requirements/Yields:

Mass in (tonnes):

1 Fe⁰ -->

0.79 CO₂ -->

0.32 H₂O -->

Fuel cell

Mass/energy out:

--> 2.07 FeCO₃

--> 0.04 H₂

--> 421kWh_e(tonne⁻¹ Fe hr⁻¹)

Fe/CO₂ Fuel Cell Economics:

CO₂ capture + sequestration cost =

\$0.00 (per tonne CO₂ mitigated)

IF the following costs or values are assumed:

Reactants -

Fe = \$85/tonne

H₂O = \$0.05/tonne

CO₂ = free

Products -

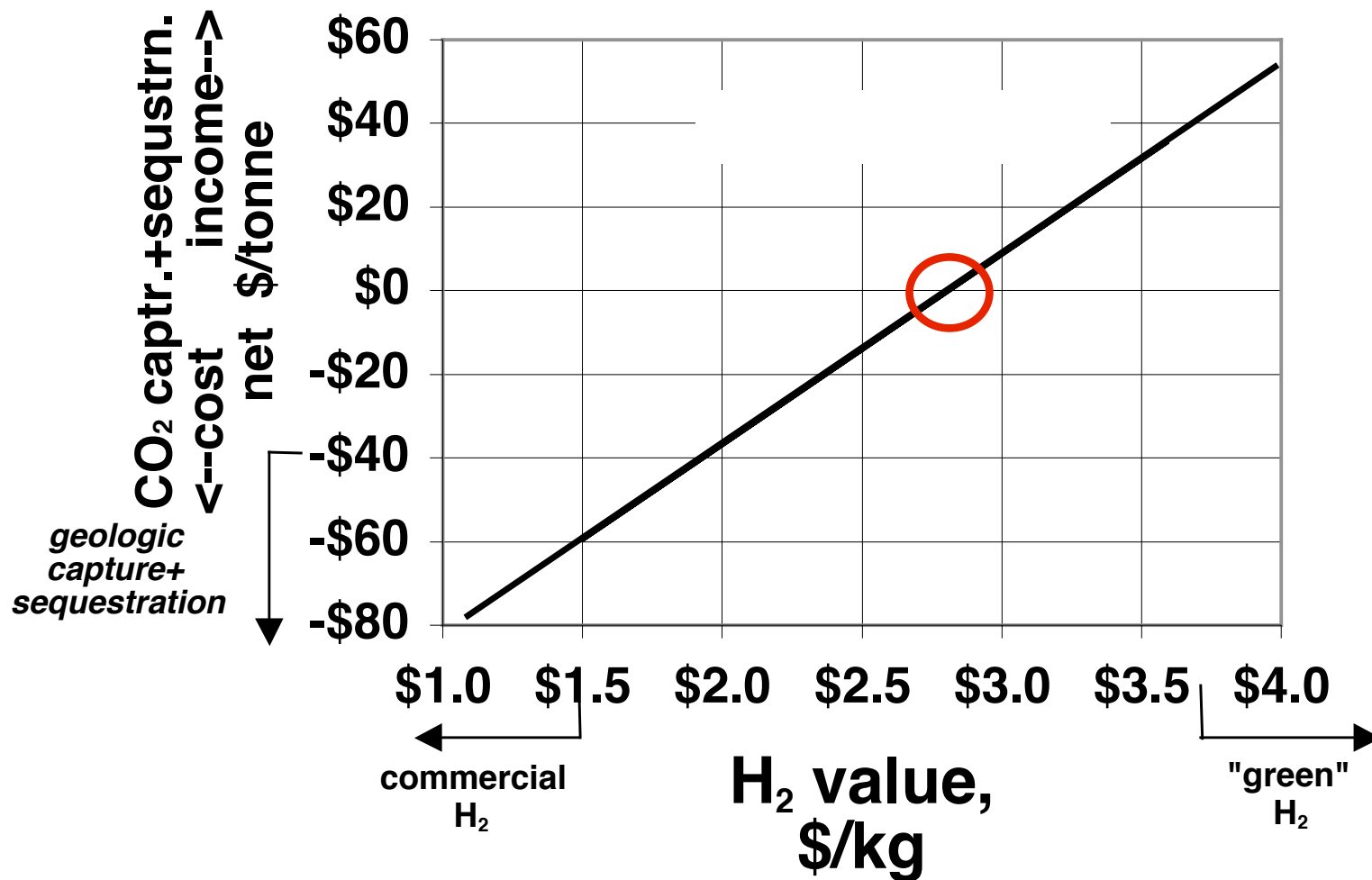
FeCO₃ = \$3.80/tonne (= \$10/tonne CO₂ credit)

H₂ = \$2,800/tonne (\$2.80/kg)

Electricity = \$0.05/kWh_e

Overhead = \$50.00/tonne Fe reacted

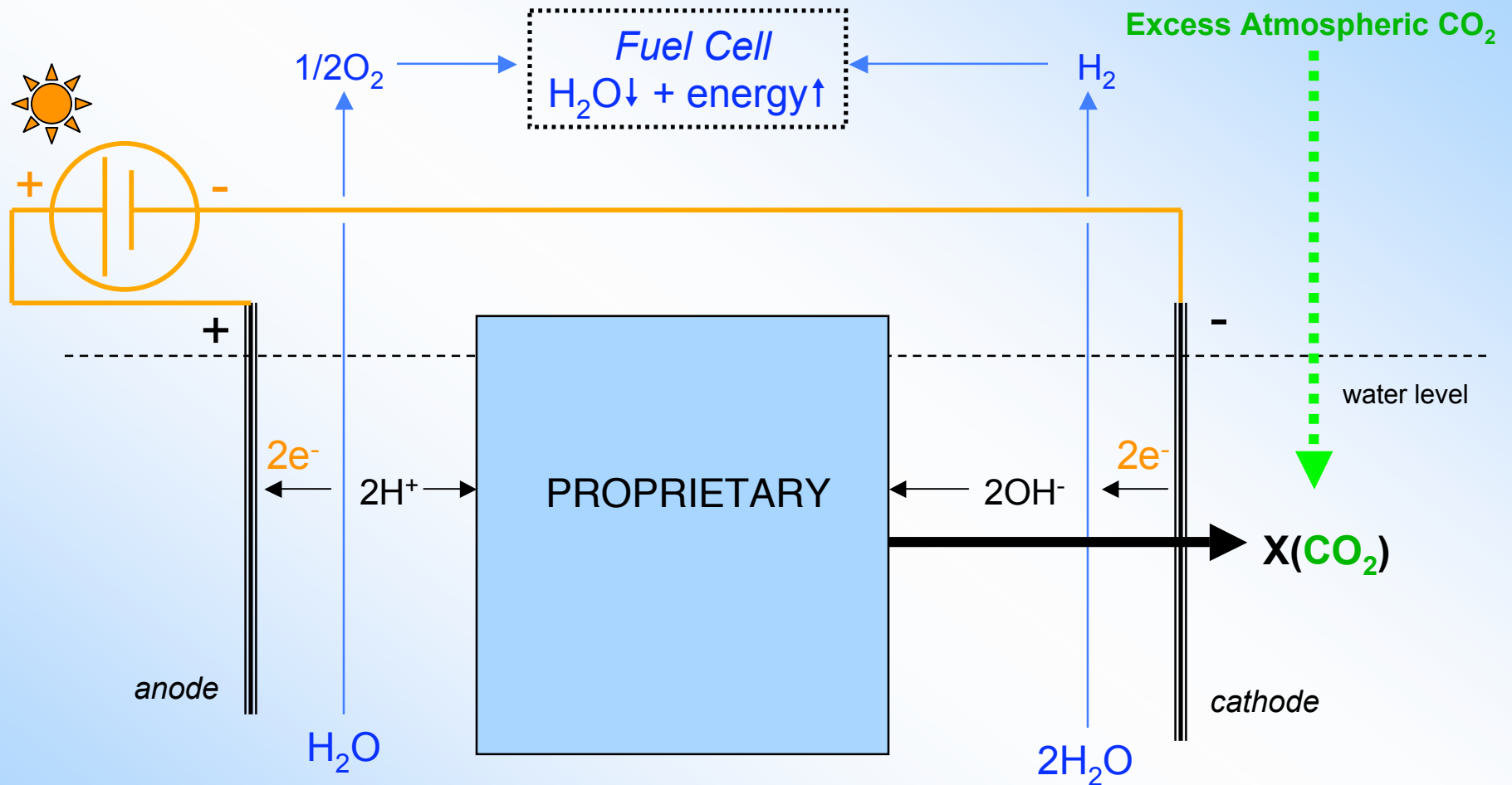
Fuel Cell Net Cost or Profit?



The Holy Grail of Sequestration: Cost-Effective Capture + Storage of CO₂ from Air

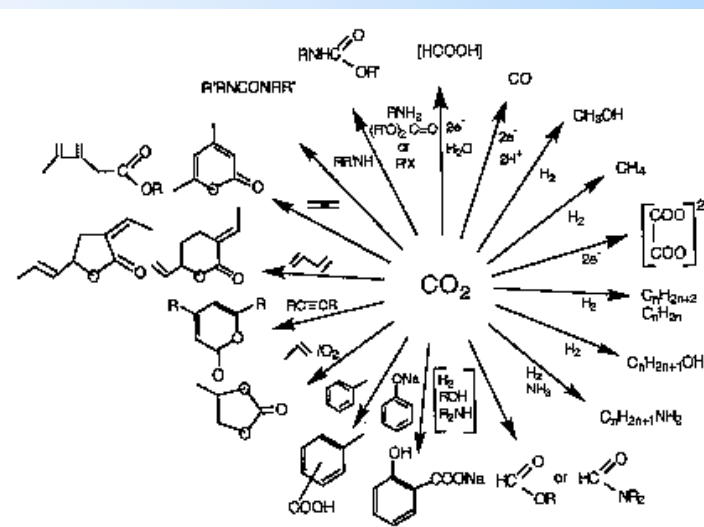
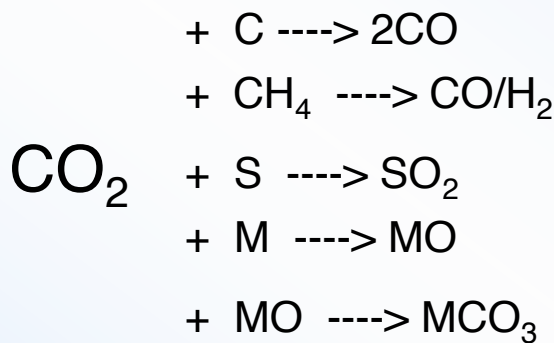
- ❑ Would allow continued fossil fuel use via post-emission mitigation of point, non-point, and mobile CO₂ emissions.
- ❑ Contrasts with current CA mitigation policy/strategy;
 - stabilizes atmos CO₂ by consuming air CO₂ not by reducing CO₂ emissions.
- ❑ Biological and chemical capture of CO₂ from air is well known (e.g., $\text{CaOH} + 2\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{HCO}_3)_2$), but:
 - photosynthesis is land-intensive; products not stable
 - hydroxides are costly and carbon/energy- intensive to make.
- ❑ A more efficient electrochemistry strategy? --->

Electrolysis with CO₂ Uptake from Air:



Bottom Line: The chemical reactivity of CO₂ should be exploited for CO₂ mitigation

❑ CO₂ is a reactive compound:



 Reaction requirements:

- Inexpensive, abundant reactants
- Low or no energy input
- Benign, storable/useable products
- Low cost/benefit

Conclusions:

- ❑ CO₂ sequestration should not be ignored in California's strategy for meeting its CO₂ mitigation goals.
- ❑ Continued reliance on fossil fuels in a carbon-constrained world (and State) will require that CO₂ sequestration technologies be found and deployed in the coming decades.
- ❑ Cost-effective and safe chemical CO₂ sequestration options are available, but need to be further researched and evaluated.
- ❑ Partners and funding for R&D are needed.

Thanks To:

Ken Caldeira, LLNL now Carnegie Inst.

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Bill Langer, USGS

Julio Friedmann, LLNL

Further Information:

rau4@llnl.gov