Low-cost Options for CO_2 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 CO_2 sequestration is needed.
- CO_2 capture/storage options, and R&D at LLNL.
- Chemistry-based approaches for CO_2 removal from waste gas streams (and air).

Conclusions:

- CO_2 sequestration should not be ignored in California's strategy for meeting its CO_2 mitigation goals.
- Continued reliance on fossil fuels in a carbon-constrained world (and State) will require that CO_2 sequestration technologies be found and deployed in the coming decades.
- Cost-effective and safe chemical CO_2 sequestration options are available, but need to be further researched and evaluated.
- Partners and funding for R&D are needed.

Why CO_2 Mitigation? It's Not Just Because of Climate Impacts!

Adding CO_2 to the Atmosphere adds CO_2 to the ocean
= Ocean Acidification:

Air-to-sea diffusion of CO_2 into seawater:

$$CO_2 + H_2O \longleftrightarrow H_2CO_3 \longleftrightarrow H^+ + HCO_3^- \longleftrightarrow 2\,H^+ + CO_3^{2-}$$

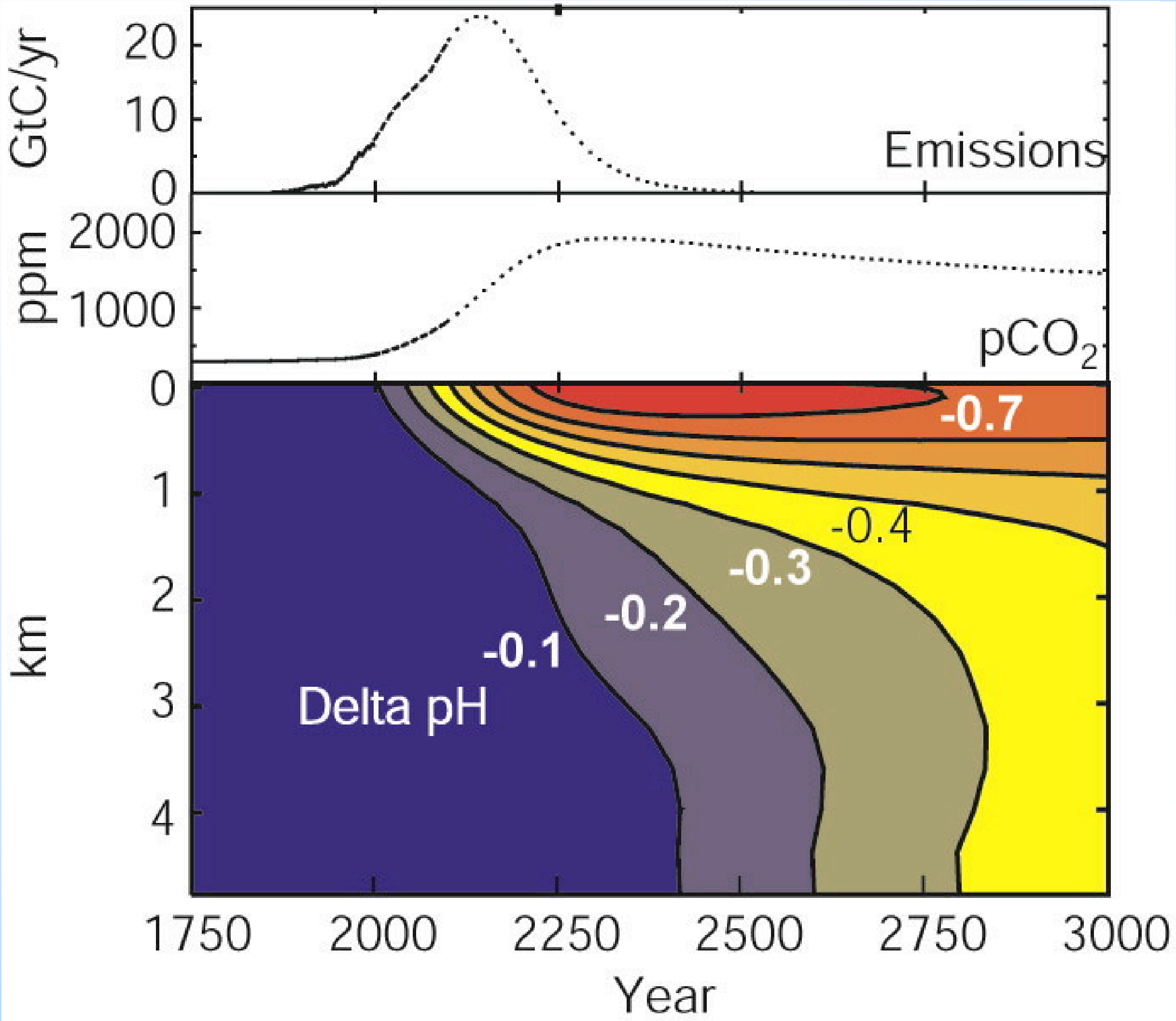
Fate of CO_2 added: (+ 9 %) (+151 %) (– 60%)

ocean relationships: $[CO_2]\uparrow$ $[H^+]\uparrow$ $pH\downarrow$ $[CO_3^{2-}]\downarrow$

➔ **For each mole of CO_2 added ~0.9 mole H^+ is produced.**

Therefore, the annual net ocean uptake of 2Gt C (=7.3Gt CO_2) produces about 0.15Gt of H^+.

CO_2 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 CO_2

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

Nature **407**: 364-

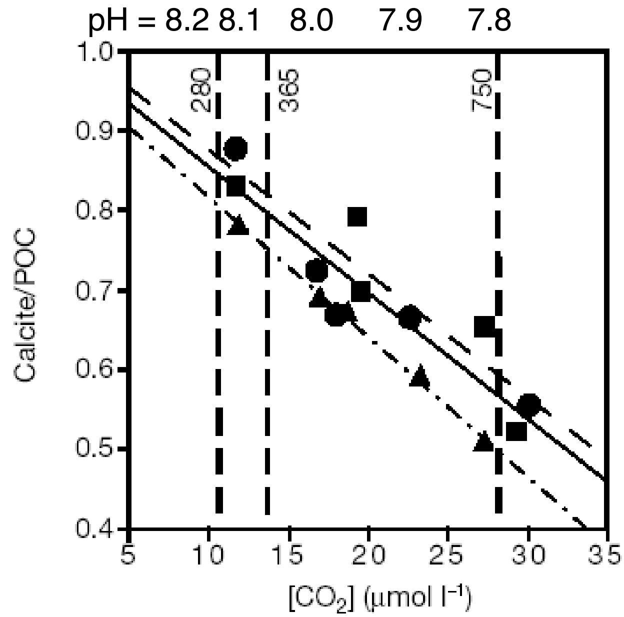


Figure 2 Ratio of calcification to POC production (calcite/POC) of *Emiliania huxleyi* as a function of CO_2 concentration, [CO_2]. Cells were incubated at photon flux densities of 30, 80 and 150 $\mu mol\ m^{-2}\ s^{-1}$ (denoted by circles, squares and triangles and corresponding solid, dashed, dash-dotted regression lines, respectively). Bars denote ±1 s.d. ($n = 3$); lines represent linear regressions. Vertical lines indicate p_{CO_2} values of 280, 365 and 750 p.p.m.v.

State Response to CO_2 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

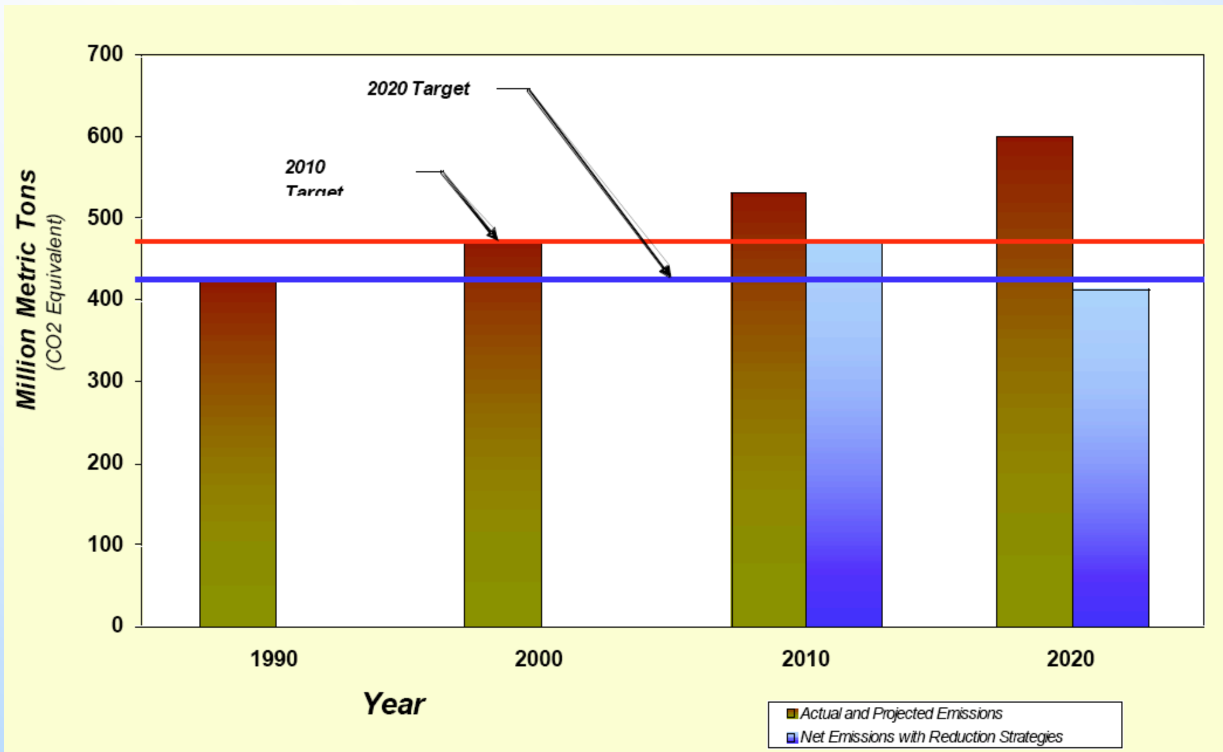
S-3-05

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 $MMTCO_2e$/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 CO_2 avoided.*
  - *Does not require participation by electricity production and oil refining.*
  - *No mention of CO_2 sequestration.*
- *The total emissions target can be achieved at no cost to consumers if additional emissions reduction cost no more than $123/tonne CO_2 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.

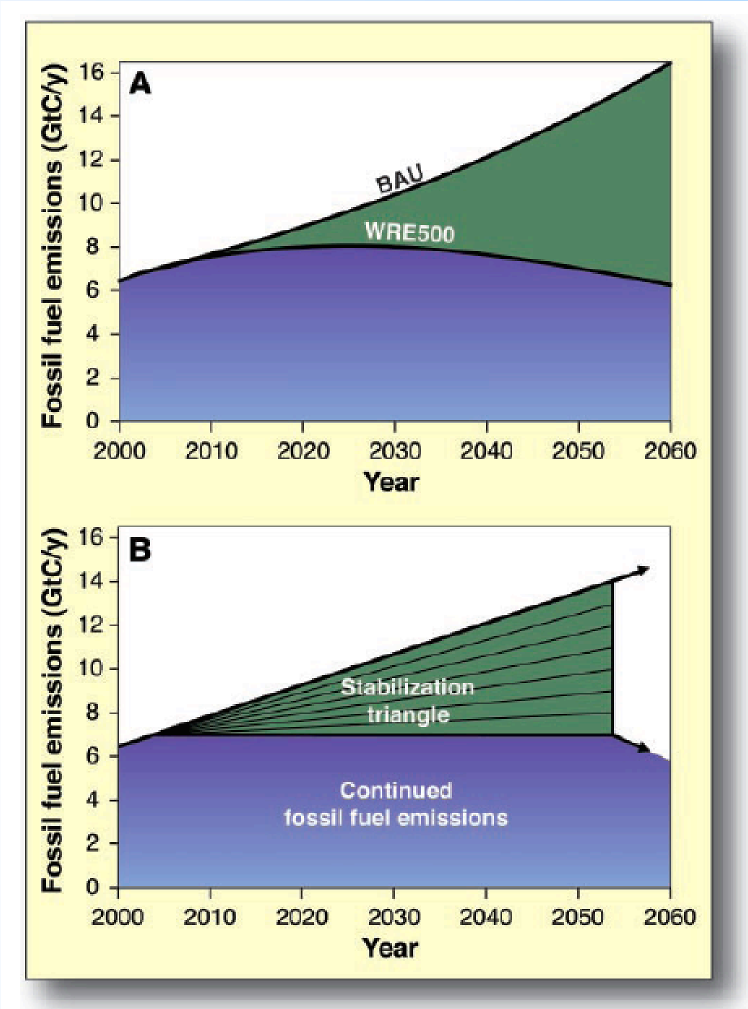
- *Includes mitigation of non-CO_2 GHG's*
- *Anticipated low net cost, and positive effects on economy*
- *No mention of CO_2 sequestration.*

How to Stabilize Atmospheric CO_2 - A Less Rosy View

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

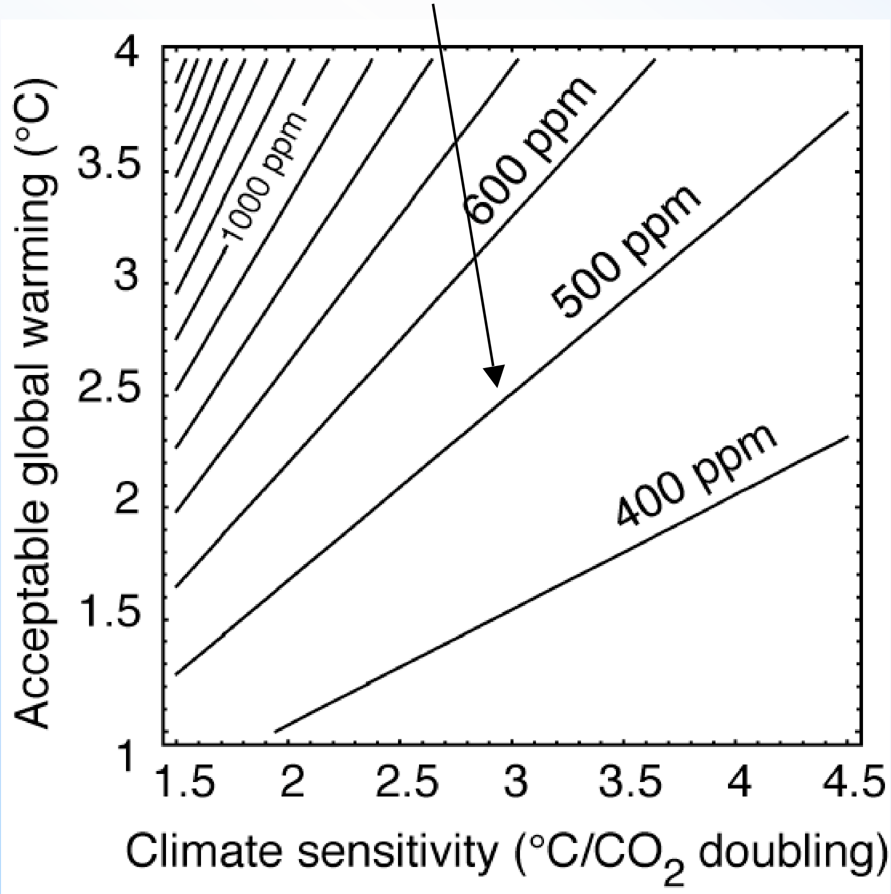
To stabilized atmospheric CO_2 at 500 ppm by 2054 -

- *Emissions must be reduced by 1/3 over the next fifty years.*
- *Draconian application of existing/known technologies is required, including CO_2 sequestration, especially in the context of hydrogen and coal-to-synfuels production.*

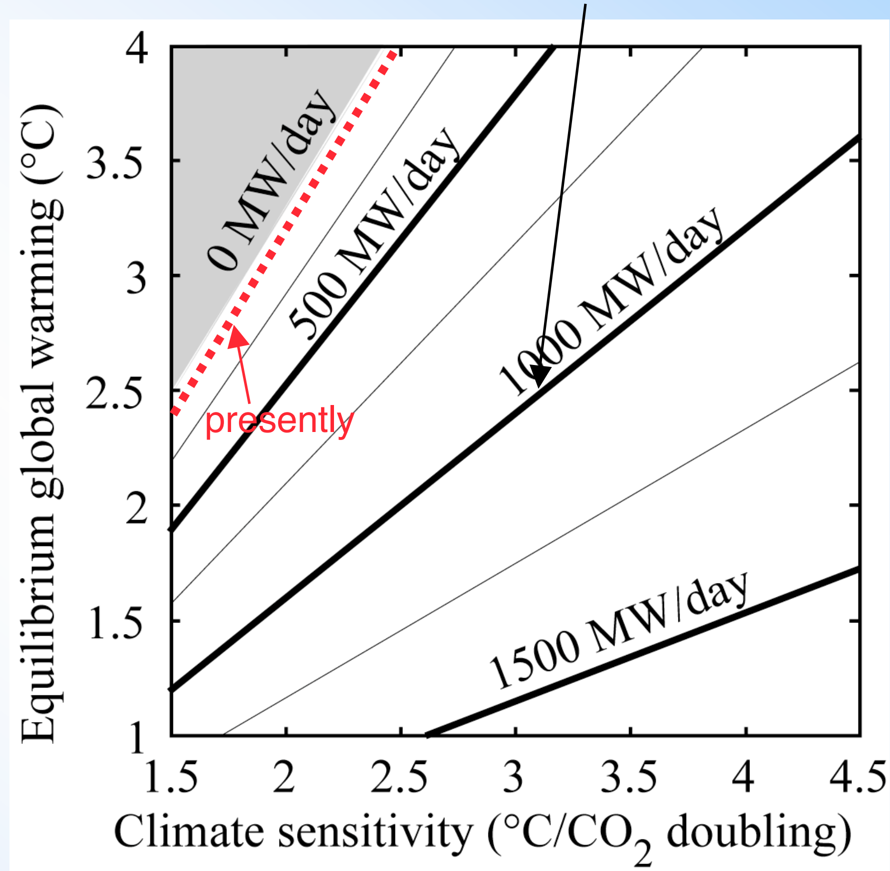


50-yr Projected pCO_2 and CO_2-Free Energy Requirements for Various Climate Sensitivities and Global Warmings:

Required Stabilized Atmos. pCO2



Required Rate of CO_2-Free Energy Addition



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

To add 1 GW_t of CO_2 Free power capacity each day:

- Biomass @ 5 W / m^2
  - 200 km^2 land area suitable for agriculture each day
- Wind @ 30 W_e / m^2
  - 20 km^2 suitably windy land area each day (~500 wind turbines per day) [+ storage and distribution]
- Solar @ 66 W_e / m^2
  - 5 km^2 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 CO_2 sequestration appears essential.**

Nordex 2.5 MW
80 m rotor diam

The Role of CO_2 Sequestration in California?

CO_2 sequestration should be include in California's CO_2 mitigation portfolio because:

- It would reduce the need for efficiency, renewables, and forest/ag management to satisfy all CO_2 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 CO_2 mitigation technologies.

CO_2 Capture/Sequestration Options:

- Land-Based
  - Abiotic molecular CO_2 capture and purification with underground (geologic) storage
  - Enhanced biological uptake/storage - managed forests, crops, microbes, soils, etc
  - Carbonation/mineralization reactions
- Ocean-Based
  - Abiotic CO_2 capture plus direct CO_2 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

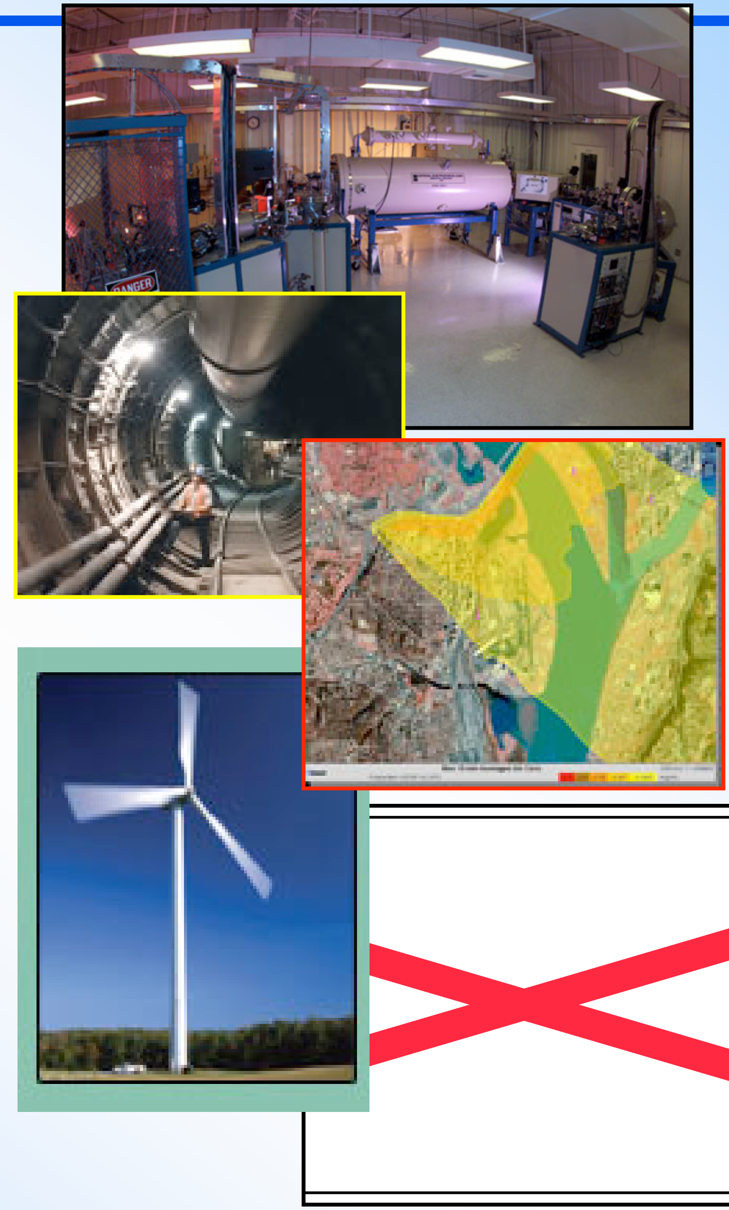
ESSE comprises for program elements

- 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

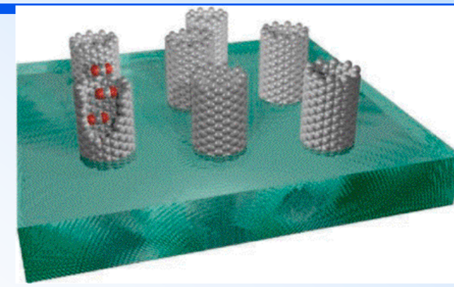
Service to government institutions and decision making process

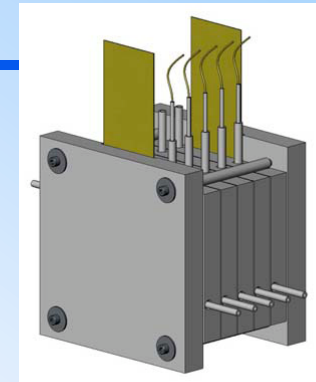


Carbon Management Program Foci:

Novel CO_2 Capture

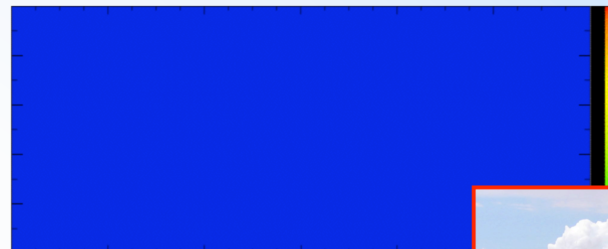
- Advanced membranes
- Accelerated Limestone Weathering
- Desalination and CO_2 Separation
- Direct Carbon Fuel Cell

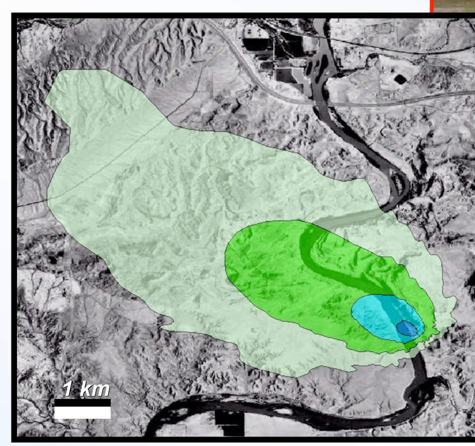




CO_2 storage in geological formations

- Simulation (and experimentation)
  - Geomechanical effects
  - Reactive chemistry (e.g., groundwater)
- CO_2 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 CO_2 Capture and Storage:

Nature's own mechanisms:

Atmospheric CO_2

<u>Photosynthesis</u>

$nCO_2 + nH_2O$ + photons

---> $(CH_2O)n + nO_2$

<u>Weathering Reactions</u>

e.g.:

CO_2 + Ca/Mg$OSiO_2$ --->

Ca/Mg$CO_3 + SiO_2$

$CO_2 + H_2O + CaCO_3$ --->

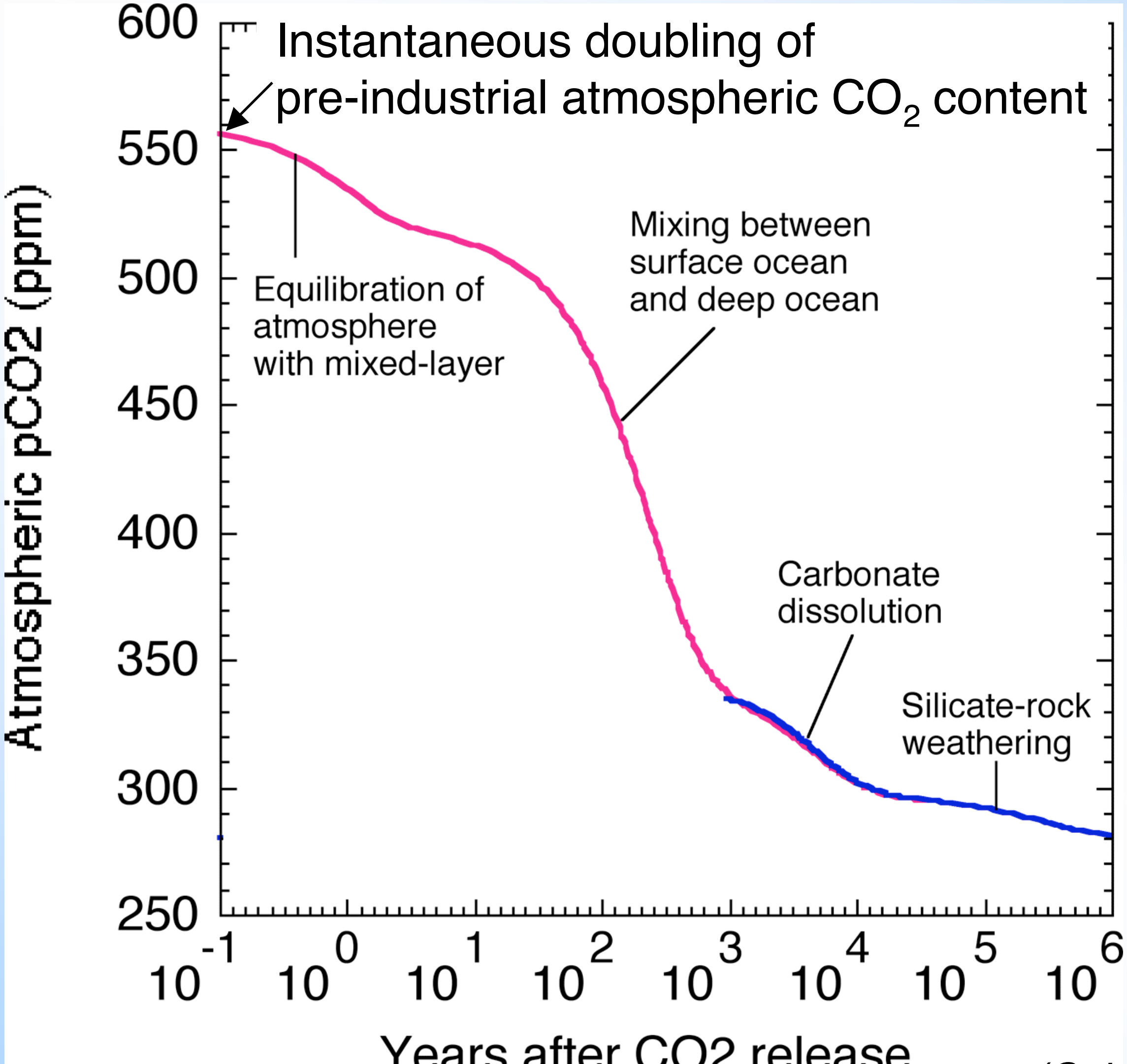
$Ca^{2+} + 2HCO_3^-$

<u>Ocean uptake</u>

$CO_2 + H_2O + CO_3^{2-}$

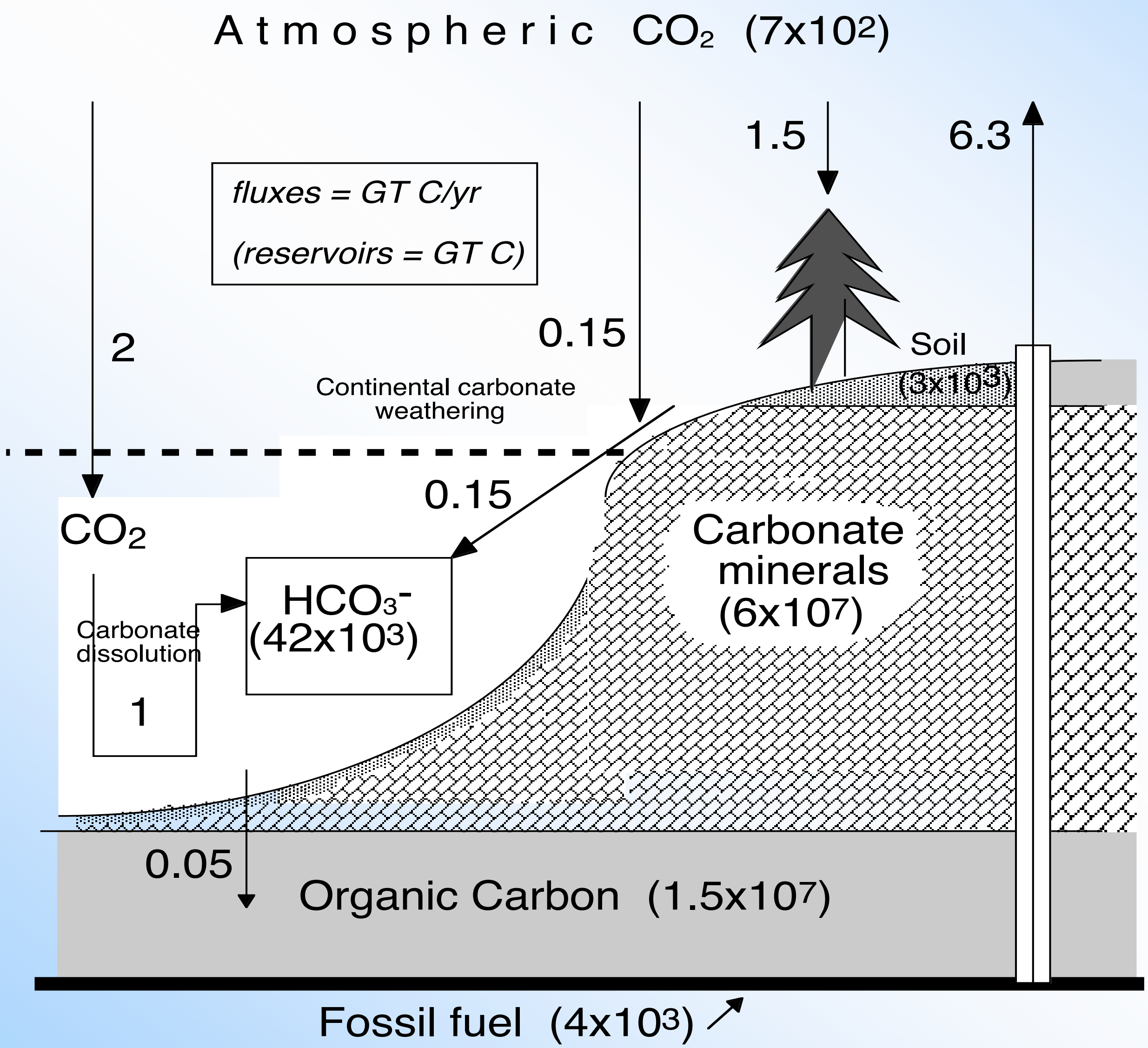
---> $2HCO_3^-$

Natural CO_2 "Capture and Sequestration":

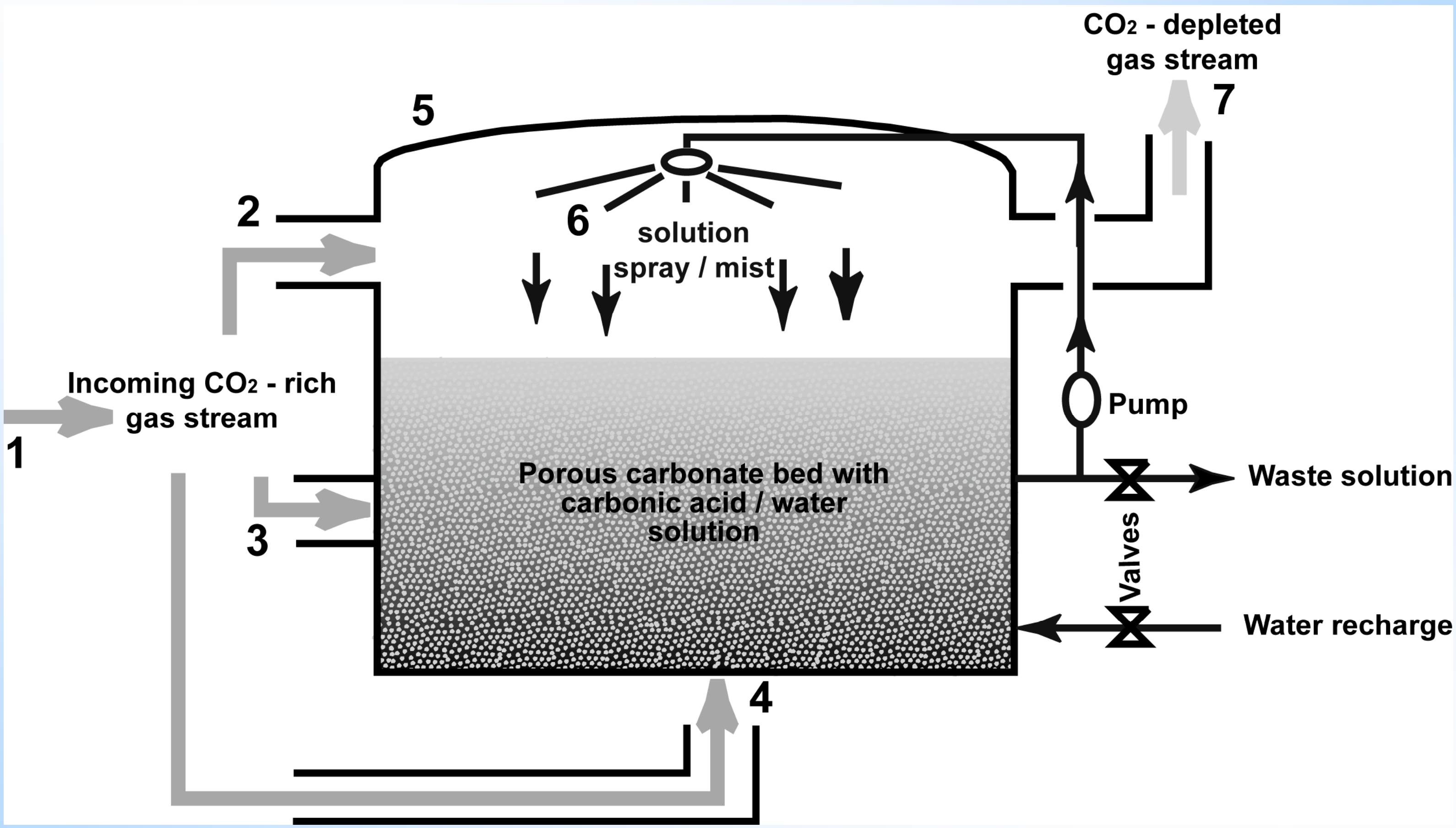


(Caldeira and Rau, 2000)

Carbonate Weathering in the Global Carbon Cycle:



Accelerated Weathering of Limestone (AWL) Reactor:



(Rau and Caldeira, 1999)

Analogies to Flue Gas Desulfurization:

FGD:

$SO_{2(g)} + H_2O_{(l)} + CaCO_{3(s)} \text{ ---> } CaSO_{3(aq)} + CO_{2(g)} + H_2O_{(l)}$

$CaSO_{3(aq)} + 0.5O_2 \text{ ---> } CaSO_{4(s)}\downarrow$

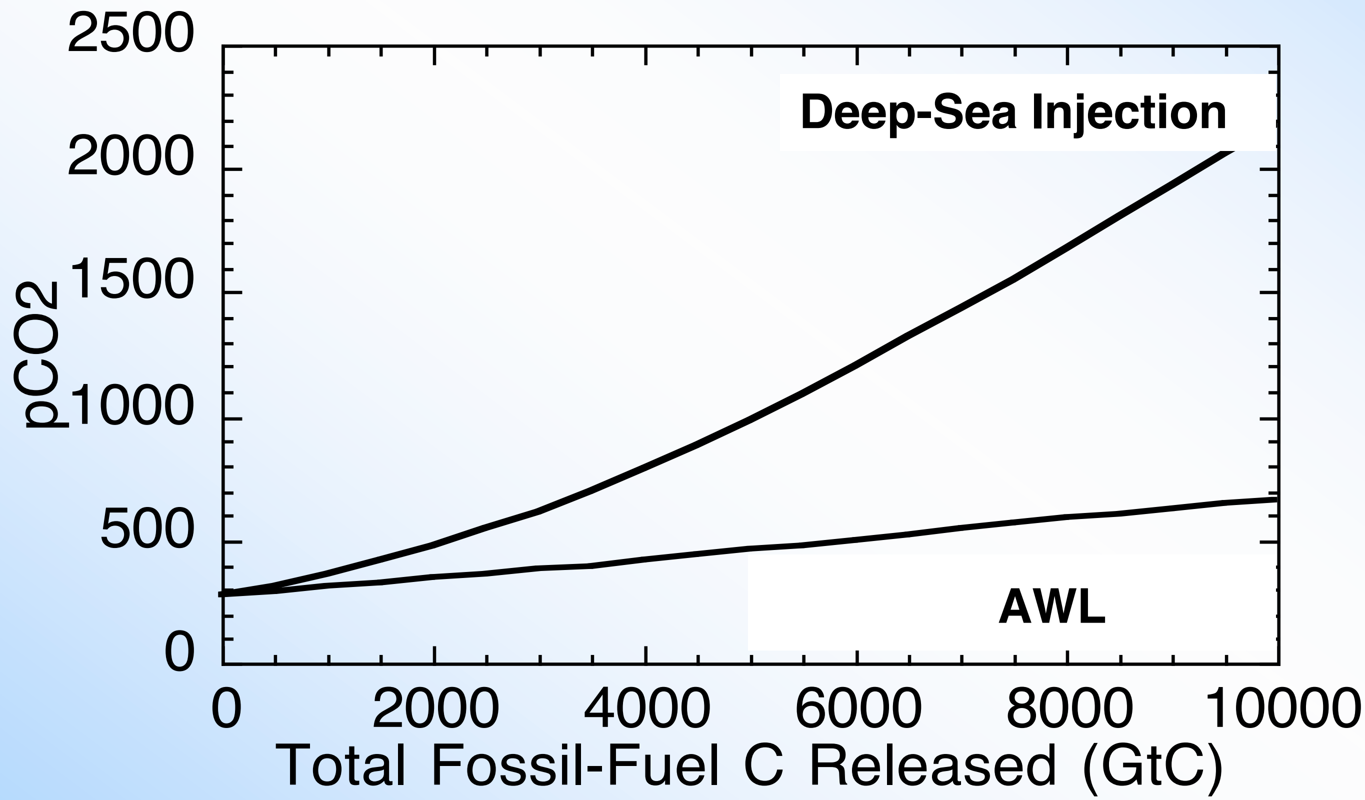
AWL:

$CO_{2(g)} + H_2O_{(l)} + CaCO_{3(s)} \text{ ---> } Ca^{2+}_{(aq)} + 2HCO_3^-{}_{(aq)}$

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

Direct CO_2 Injection vs AWL - Effect on Atmospheric pCO_2:

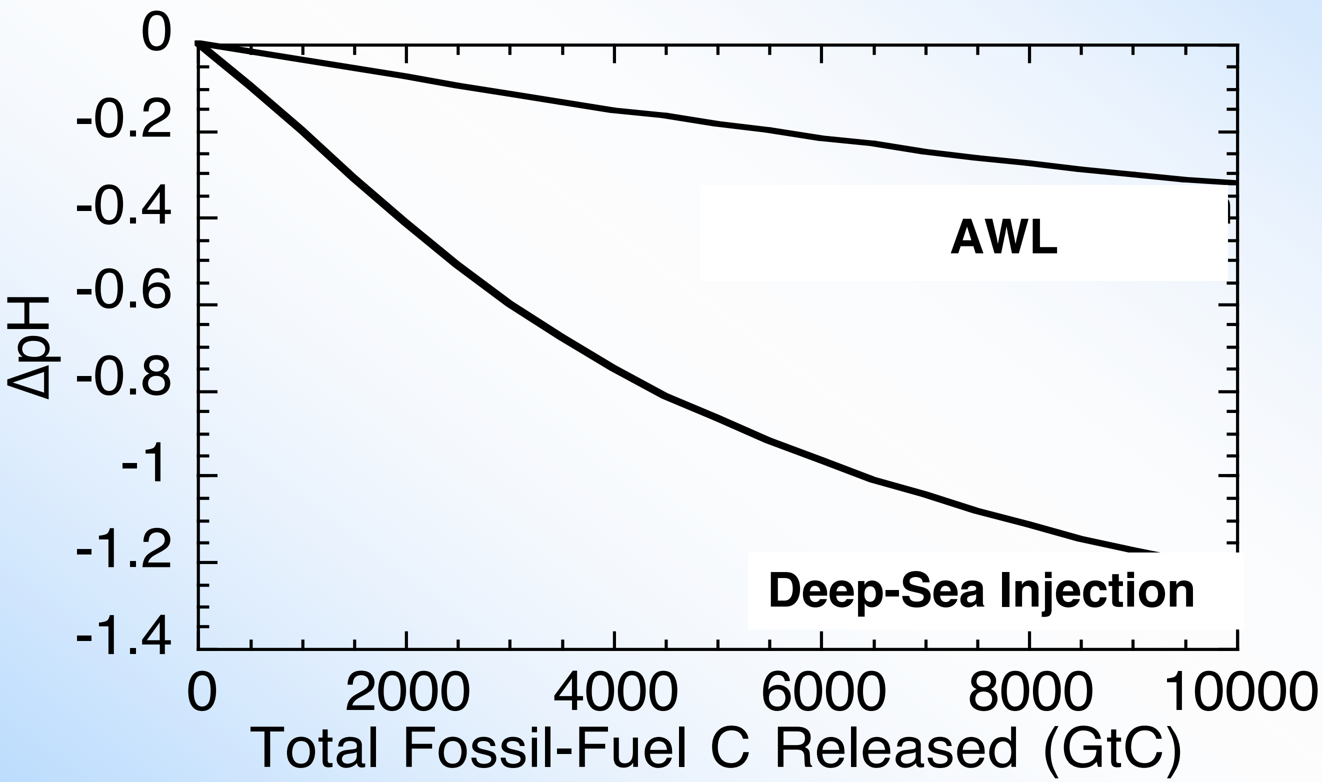
Atmospheric pCO2 after 1,000 years:



(Caldeira and Rau, 2000)

Direct Injection vs AWL -Effect on Ocean pH:

Ocean pH after 1,000 years:



(Caldeira and Rau, 2000)

AWL Economics:

- Estimated cost per tonne CO_2 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
  - Capital and maintenance = $ 2.50

TOTAL: **$ 29/tonne CO_2**

Compared to $40-$60/tonne for amine capture + geologic storage of CO_2 from a conventional power plant

Optimum AWL Economics:

Estimated cost per tonne CO_2 sequestered, assuming coastal location:

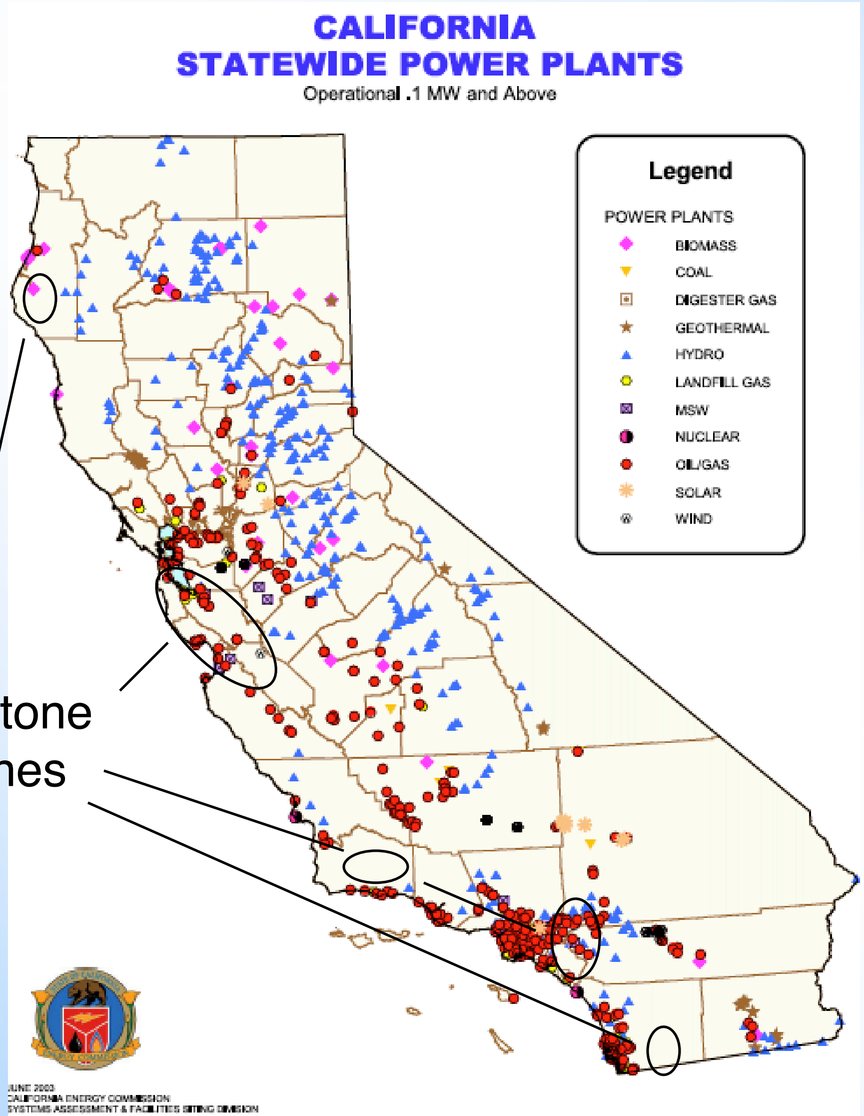
- Limestone -
  - 2.3 tonnes @ $4/tonne = ~~$ 9.20~~ *use free, nearby waste limestone*
  - crushing from 10 cm to 1cm = ~~$ 1.45~~
  - transport 100 km by rail = ~~$ 8.00~~
  - Water -
  - 10^4 m^3, pumped 2 vertical meters = ~~$ 7.57~~ *use cooling water*
- Capital and maintenance = $ 2.50

TOTAL: **<$3/tonne CO_2**

Advantages of AWL:

- Abundant and cheap reactants:
  - Limestone - carbonates = 6×10^7Gt C, fossil fuels = 4×10^3Gt C;
    H_20 - ocean = $1.4 \times 10^{18} m^3$
- Relatively innocuous waste products:
  - Primarily Ca^{2+}+ and HCO_3^- in solution; Avoids low pH inherent in passive or active CO_2 injection into ocean; benefits to marine biota
- Not energy- or technology-intensive:
  - Does not require separate, costly CO_2 capture/concentration
  - Can modify existing flue gas scrubbing technology
    - analogous to coal plant desulfurization
- Relatively inexpensive
  - 10-20% US emissions mitigated at <$30/tonne CO_2

Limestone Availability vs CA Coastal Power Plant Location:



Major Limestone Deposits/Mines

Impacts/Issues Needing Further Research:

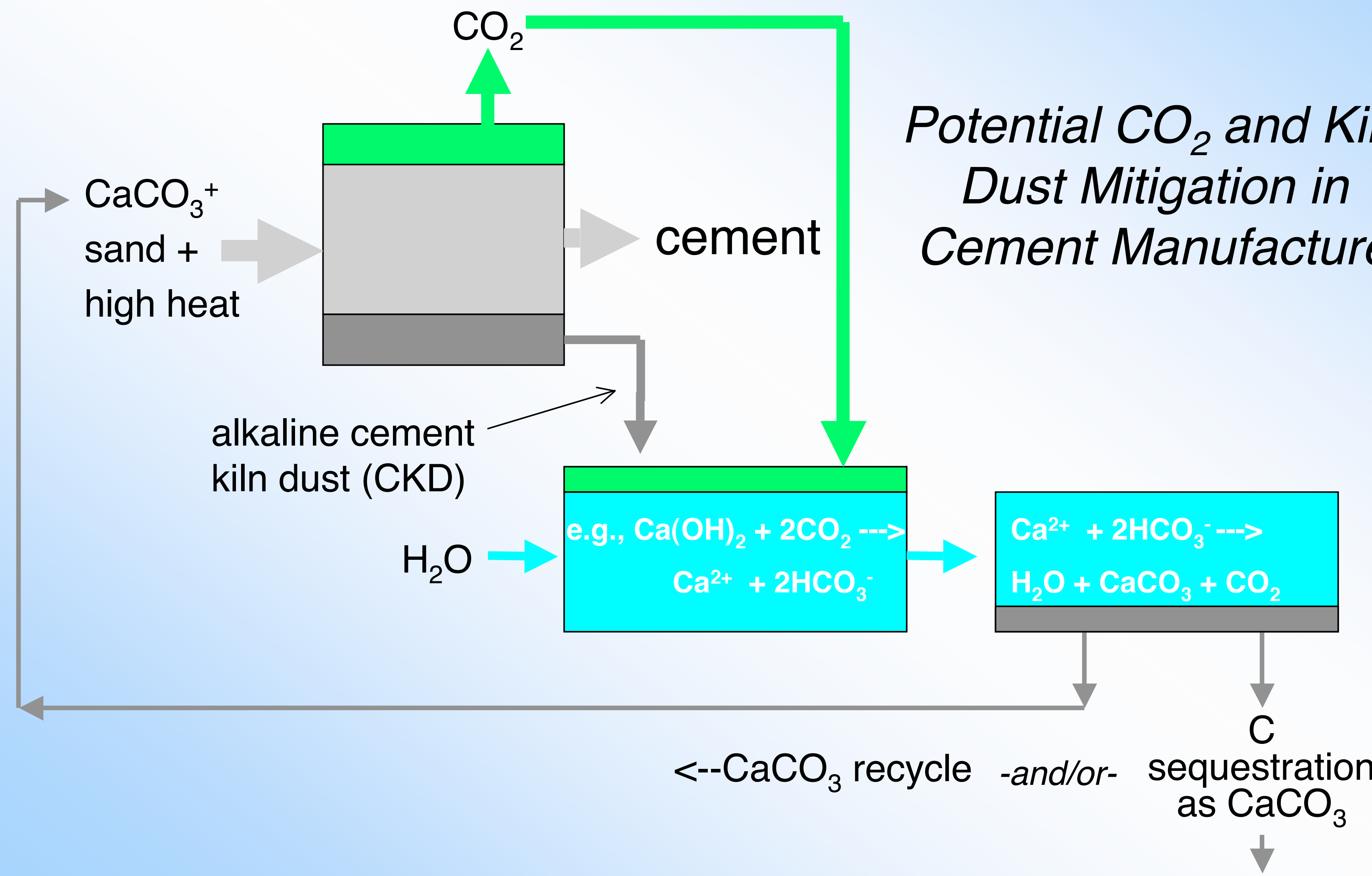
- Local availability of limestone and water limits application
  - could be offset by piping CO_2 to favorable AWL sites
  - use inland saline aquifer or water with oil?
- Marine biological impacts -
  - net beneficial?
  - trace contaminants from flue gas or limestone?
- Environmental, transportation, and economic impacts due to increased limestone mining/transport.
- Regional, national, and global assessments and R&D needed. Proposal submitted to CEC PIER program.

CO_2 Mitigation In Cement Manufacture:

CCAP Report 2005: CA Cement Manufacture -

- Current state emissions $\approx$ 10.5 MMT CO_2/yr
- Cumulative emissions by 2020 = 260 MMTCO_2
- Can be reduced by 47 MMTCO_2 by 2020 at a cost <$10/tonne CO_2 via:
  - Limestone or flyash + cement blends
  - Alternative fuels
- But there is industry/public resistance to these options
  - Alternatives needed

Combined CO_2 and Kiln Dust Mitigation:



Potential CO_2 and Kiln Dust Mitigation in Cement Manufacture

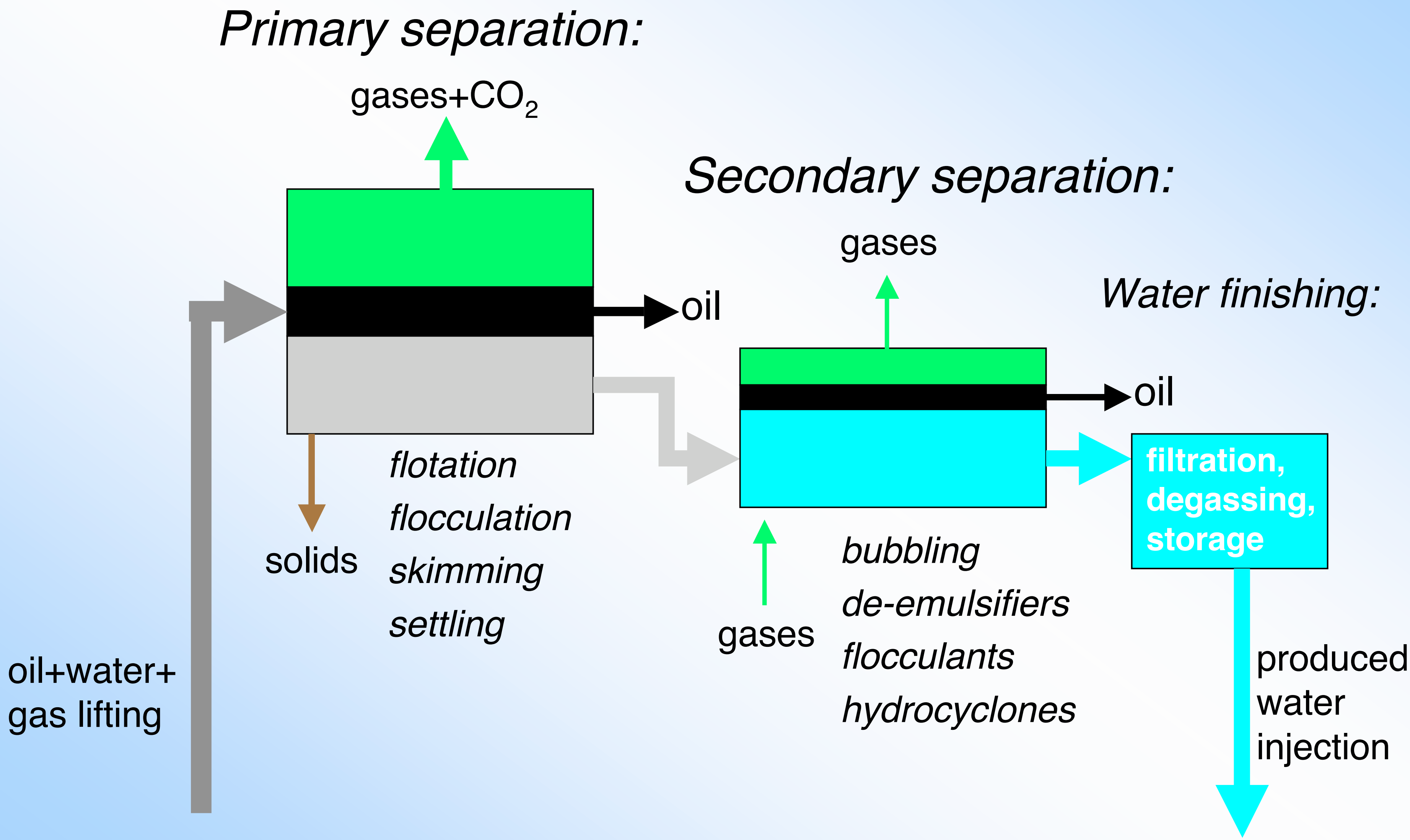
Features/Issues:

- Helps mitigate both CO_2 and CKD
- Potential co-benefits
  - Recycle of waste Ca as $CaCO_3$
  - Selective precipitation of other useful compounds e.g. K, Mg, and Na carbonates
- Should be very low cost, maybe <$1/tonne CO_2
- Further evaluation and testing needed. Proposal submitted to Portland Cement Association.

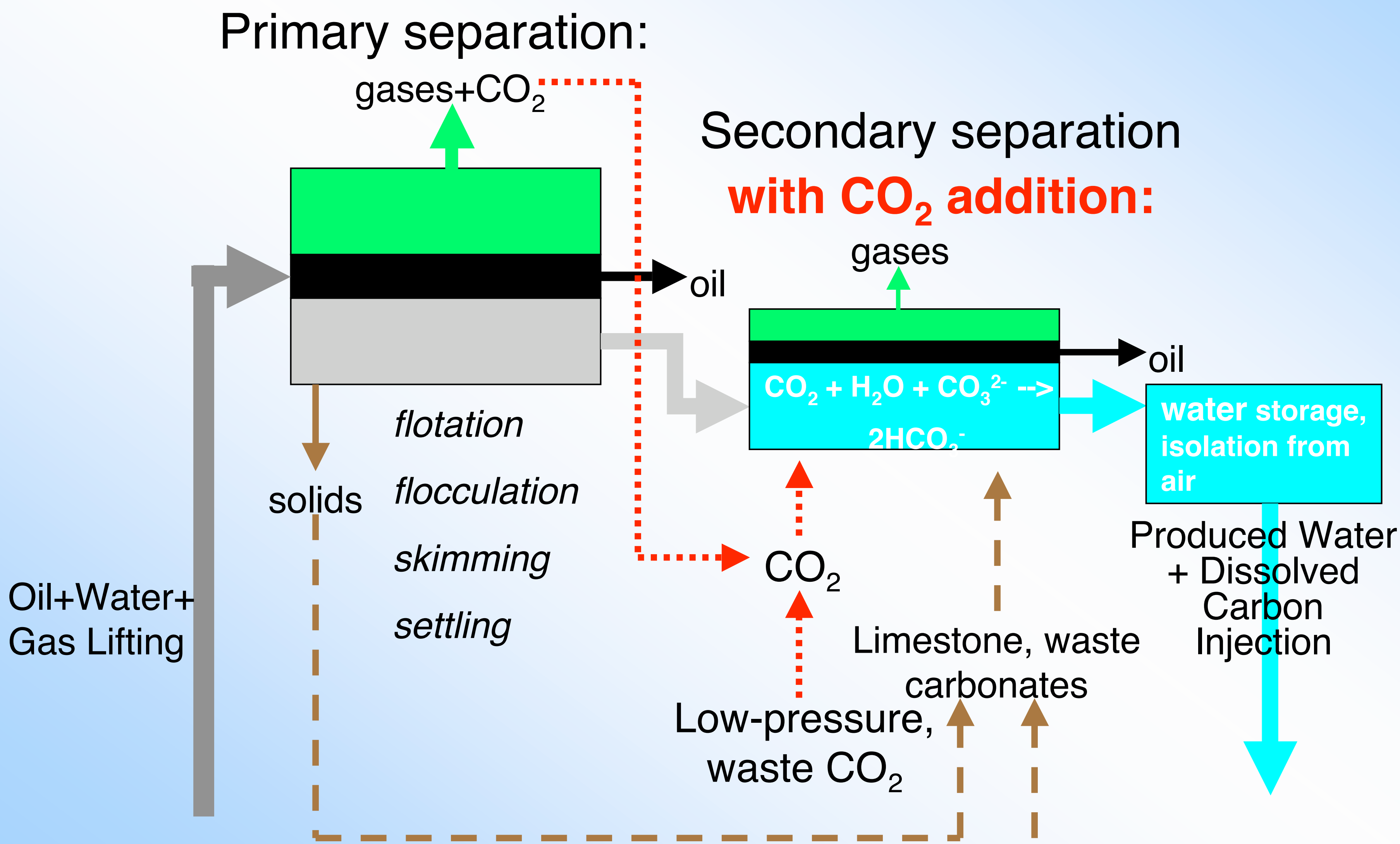
CO_2 Sequestration Using Water Co-Produced With Oil:

- 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 CO_2 waste streams (based on analysis of Texas produced waters).
- Therefore why not equilibrate these waters with waste CO_2 (+-limestone) to effect very low cost CO_2 capture and safe geologic storage? Co-benefits:
  - ➢ reduced scaling and microbial fouling
  - ➢ enhanced oil recovery and oil/water separation?

Typical Produced Water Scheme:



Produce Water with CO_2 Capture +Geologic Storage:



Another Idea: Iron/CO_2 Fuel Cells?

From corrosion science:

$$Fe^0_{(s)} + 2CO_{2(g)} + 2H_2O_{(l)} \Rightarrow Fe(HCO_3)_{2(aq)} + H_{2\,(g)}\uparrow + 113.5kJ \qquad (1)$$

$$\Delta G = -2.2kJ \text{ @ } 25°C$$

$$Fe(HCO_3)_{2(aq)} \Rightarrow FeCO_{3(s)}\downarrow + CO_{2(g)}\uparrow + H_2O_{(l)} - 52.3kJ \qquad (2)$$

Net reaction:

$$Fe^0_{(s)} + CO_{2(g)} + H_2O_{(l)} \Rightarrow FeCO_{3(s)}\downarrow + H_{2(g)}\uparrow + 61.2kJ \qquad (3)$$

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

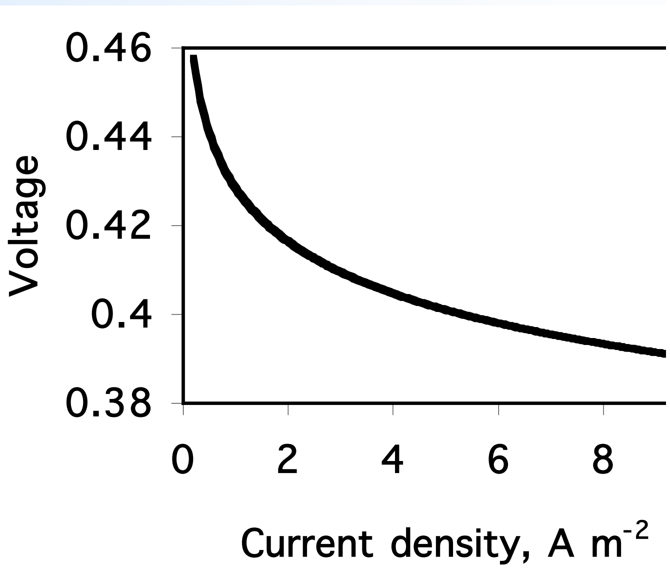
Thus, at ambient temperature and pressure:

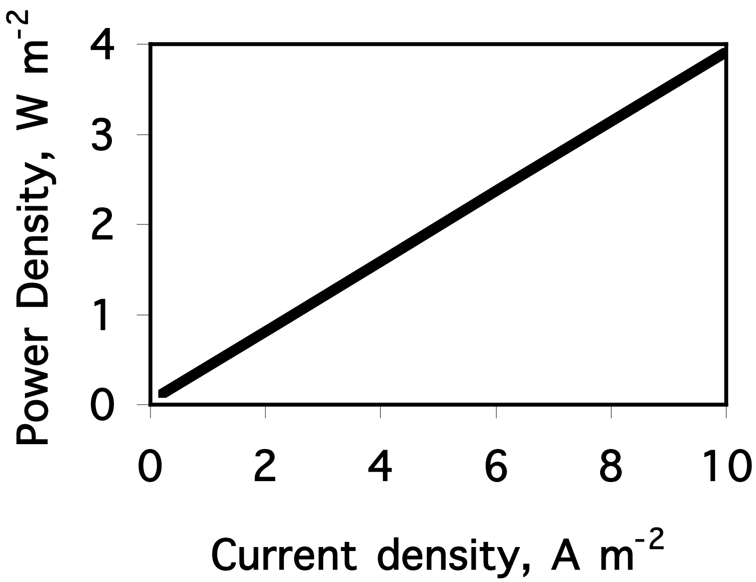
- CO_2 converted to a dissolved bicarbonate or solid carbonate
- hydrogen gas is produced
- electricity is produced ----->

Electricity Generation - an Fe/CO_2 Galvanic Cell:

- *Anodic reaction:* $Fe^o \Rightarrow Fe^{2+} + 2e^-$ (4)
- *Cathodic reaction:* $2H^+ + 2e^- \Rightarrow H_2$ (5)

e.g., from Hasenberg (1988):





Possible Fe/CO_2 Fuel Cell Design:

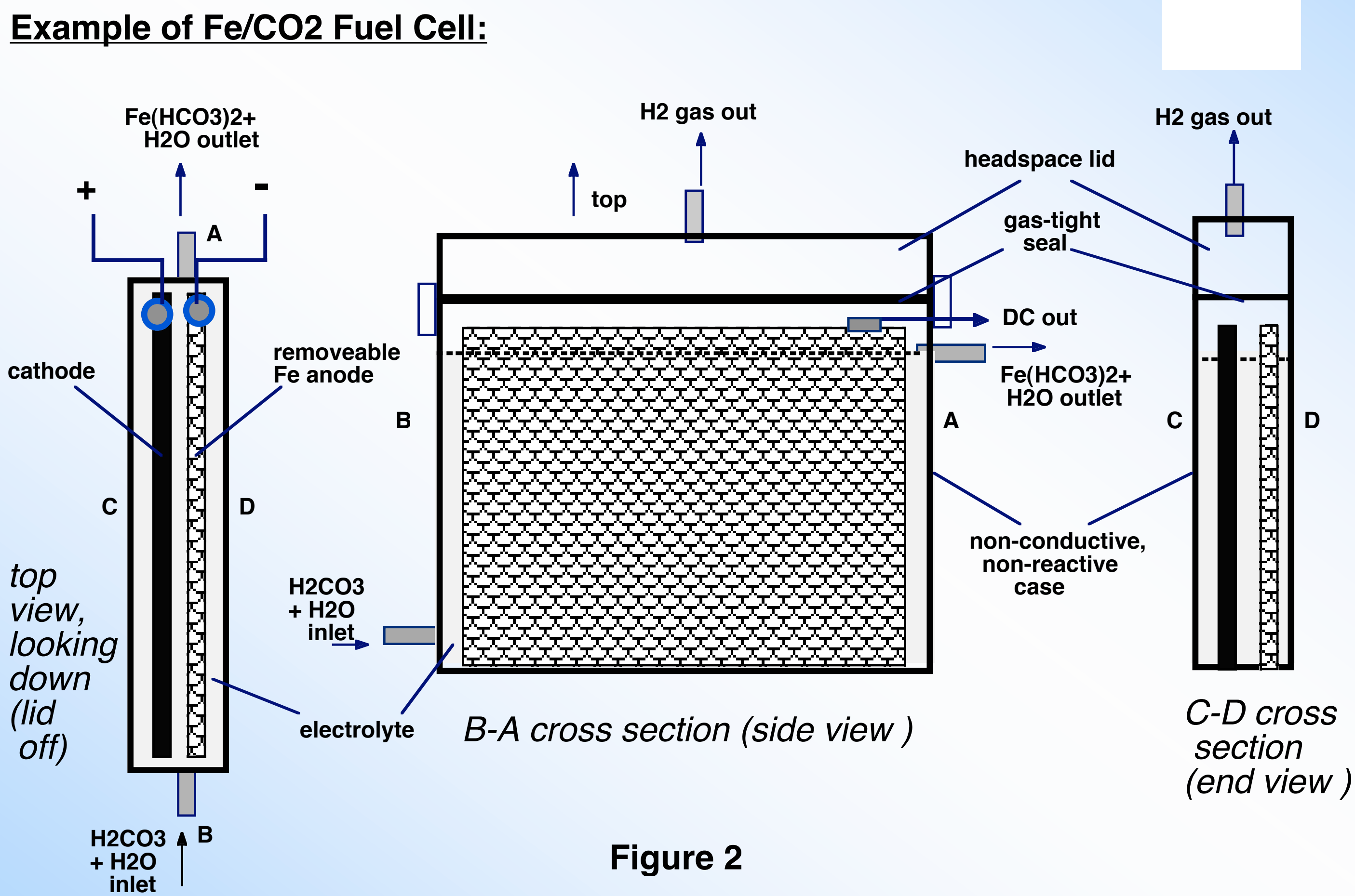


Figure 2

Large-Scale Fe/CO_2 Fuel Cell Operation:

G.H. Rau
Aug 11'03

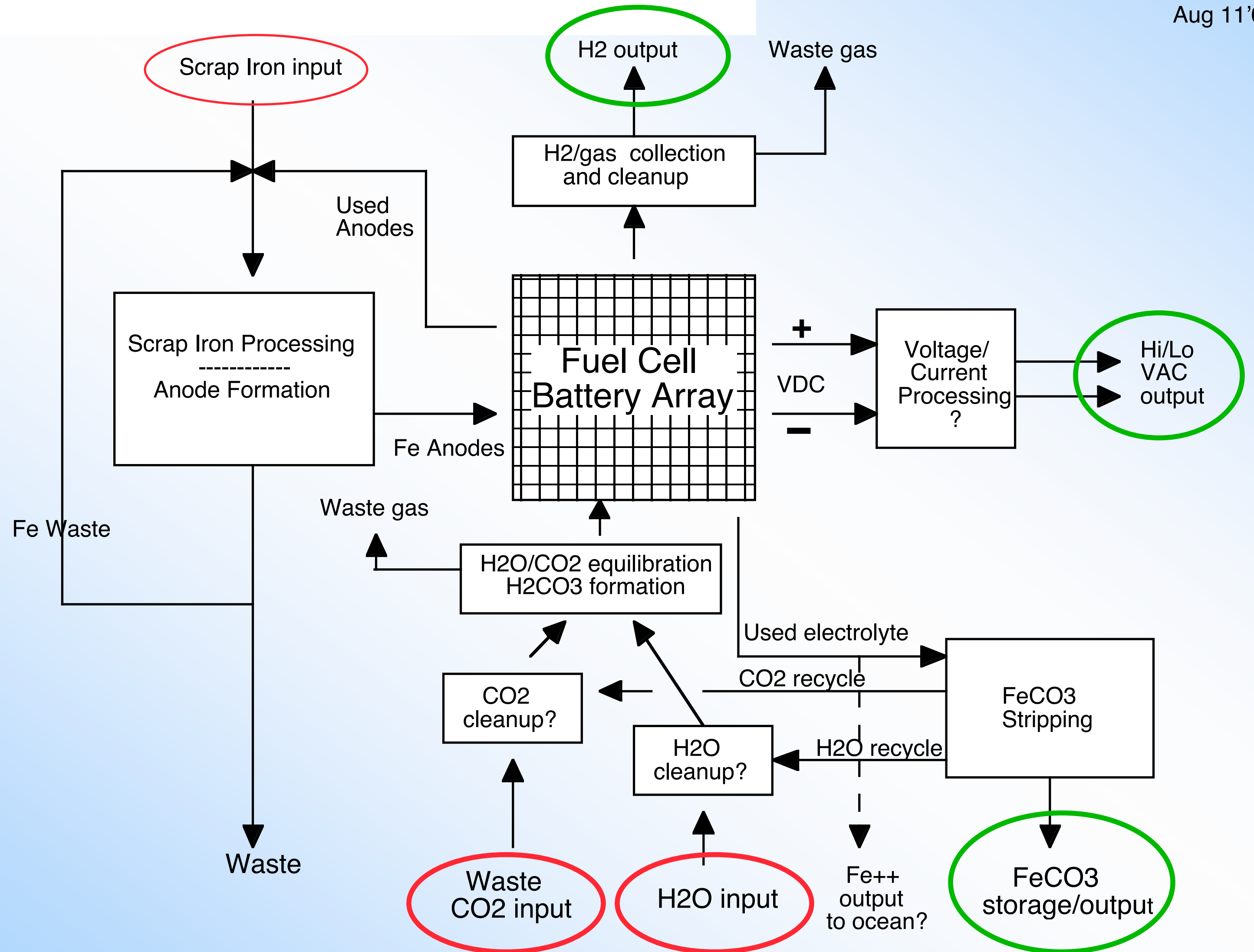


Figure 1

Fe/CO_2 Fuel Cell Requirements/Yields:

Mass in (tonnes):			*Mass/energy out:*
1 Fe^0	-->	Fuel cell	--> 2.07 $FeCO_3$
0.79 CO_2	-->		--> 0.04 H_2
0.32 H_2O	-->		--> 421 kWh_e(tonne^{-1} Fe hr^{-1})

Fe/CO_2 Fuel Cell Economics:

CO_2 capture + sequestration cost =

$0.00 (per tonne CO_2 mitigated)

IF the following costs or values are assumed:

Reactants -

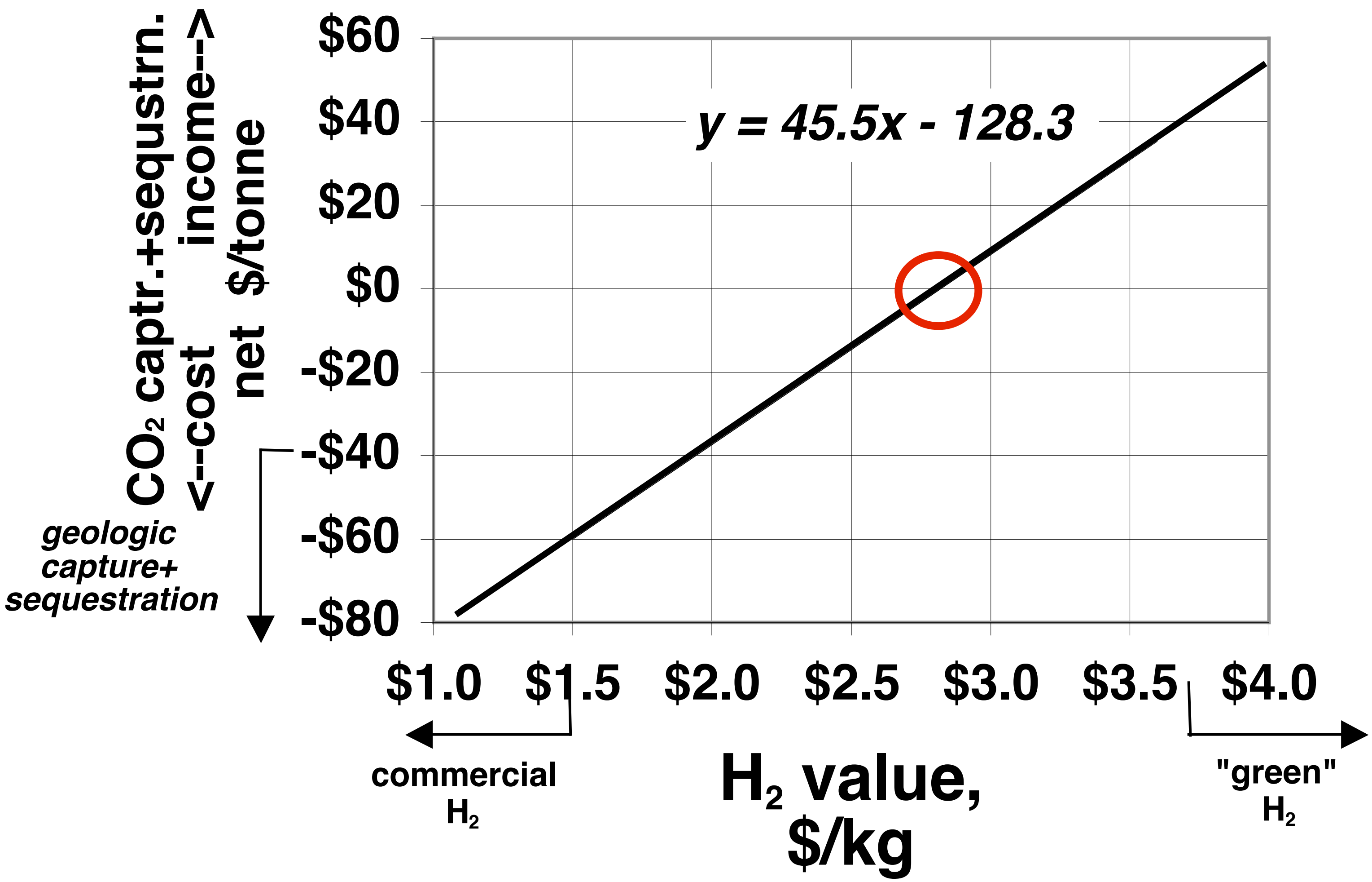
Fe = $85/tonne
H_2O = $0.05/tonne
CO_2 = free

Products -

$FeCO_3$ = $3.80/tonne (=$10/tonne CO_2 credit)
H_2 = $2,800/tonne ($2.80/kg)
Electricity = $0.05/kWh$_e$

Overhead = $50.00/tonne Fe reacted

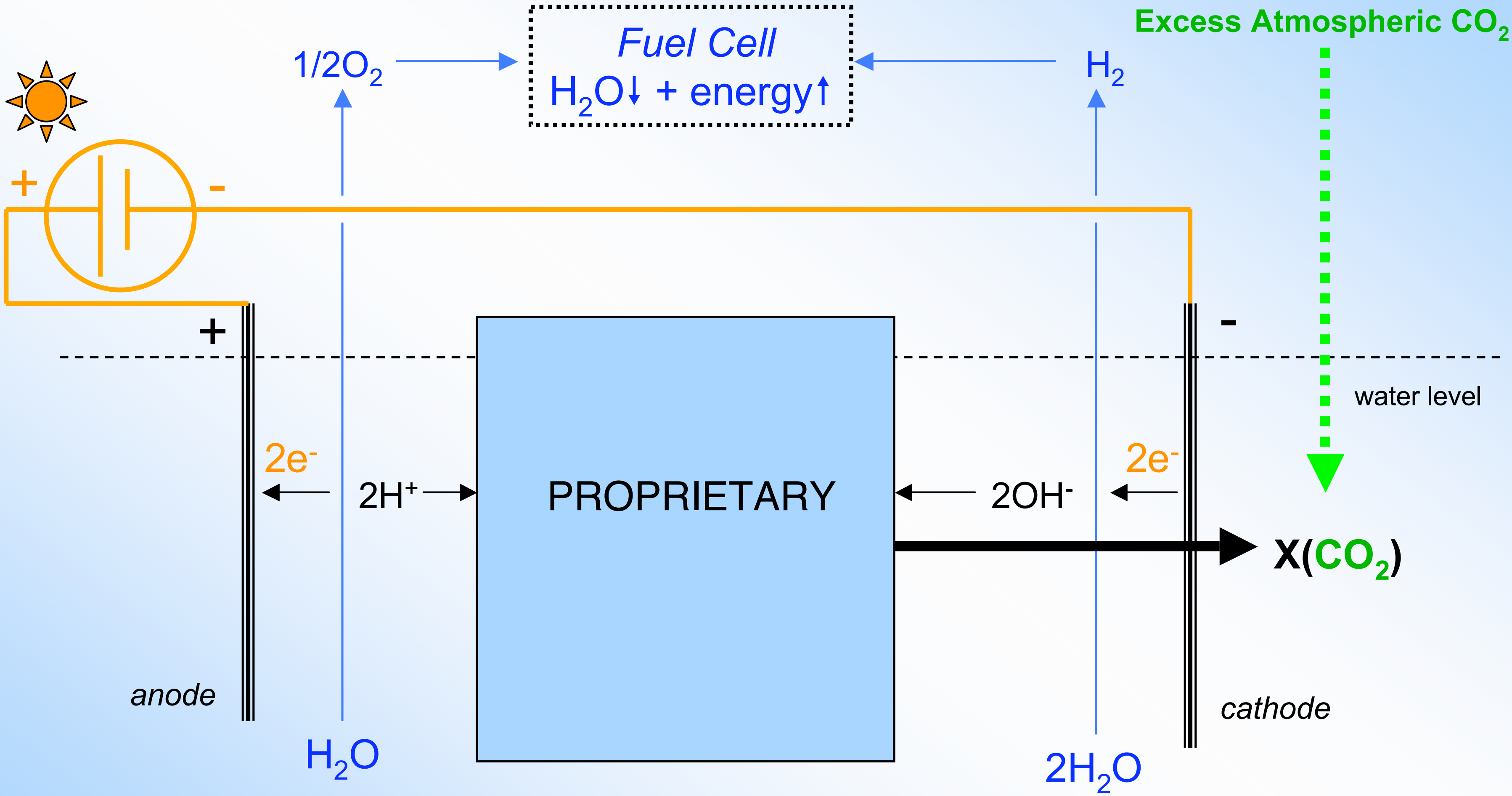
Fuel Cell Net Cost or Profit?



The Holy Grail of Sequestration: Cost-Effective Capture + Storage of CO_2 from Air

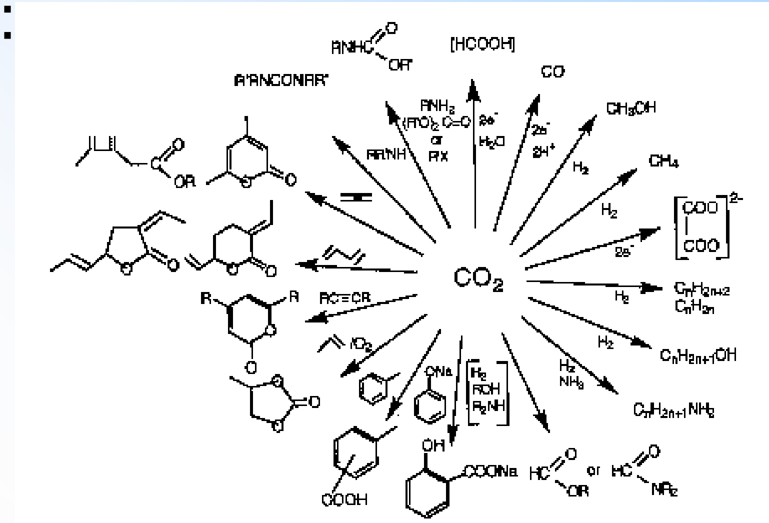
- Would allow continued fossil fuel use via post-emission mitigation of point, non-point, and mobile CO_2 emissions.
- Contrasts with current CA mitigation policy/strategy;
  - stabilizes atmos CO_2 by consuming air CO_2 not by reducing CO_2 emissions.
- Biological and chemical capture of CO_2 from air is well known (e.g., CaOH $+2CO_2+H_2O$ --> $Ca(HCO_3)_2$), but:
  - photosynthesis is land-intensive; products not stable
  - hydroxides are costly and carbon/energy- intensive to make.
- A more efficient electrochemistry strategy? --->

Electrolysis with CO_2 Uptake from Air:



Bottom Line: The chemical reactivity of CO_2 should be exploited for CO_2 mitigation

- CO_2 is a reactive compound:



CO_2

+ C ----> 2CO

+ CH_4 ----> CO/H_2

+ S ----> SO_2

+ M ----> MO

+ MO ----> MCO_3

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

Conclusions:

- CO_2 sequestration should not be ignored in California's strategy for meeting its CO_2 mitigation goals.
- Continued reliance on fossil fuels in a carbon-constrained world (and State) will require that CO_2 sequestration technologies be found and deployed in the coming decades.
- Cost-effective and safe chemical CO_2 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.

Kevin Knauss, LLNL

Bill Langer, USGS

Julio Friedmann, LLNL

Further Information:

rau4@llnl.gov