
Chemical Options for CO₂ Capture and Storage

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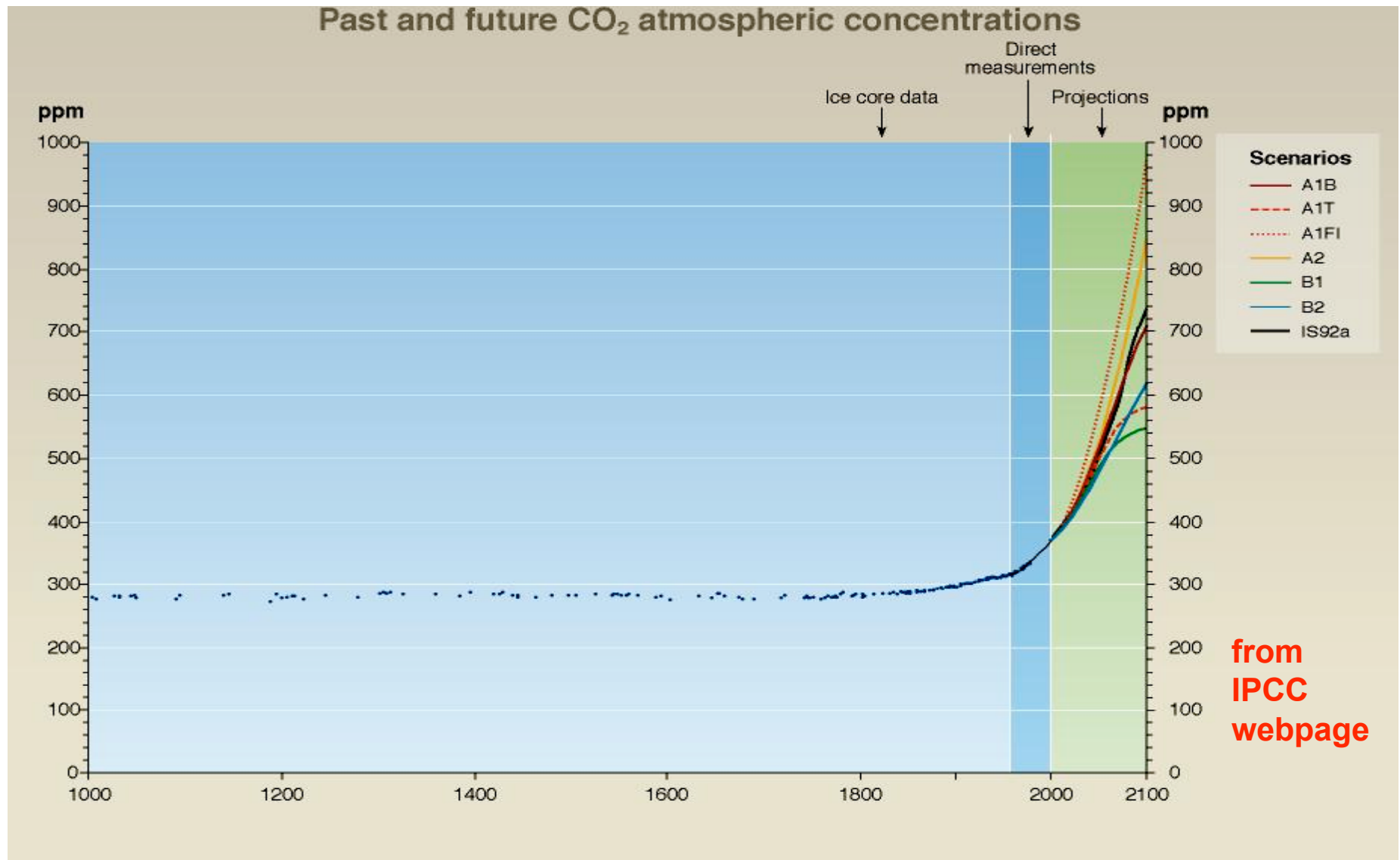
Outline:

- ❑ Why CO₂ mitigation is needed.
- ❑ Options for stabilizing atmospheric CO₂ concentration
- ❑ Some chemistry-based approaches to CO₂ sequestration, e.g., bicarbonate and carbonate formation

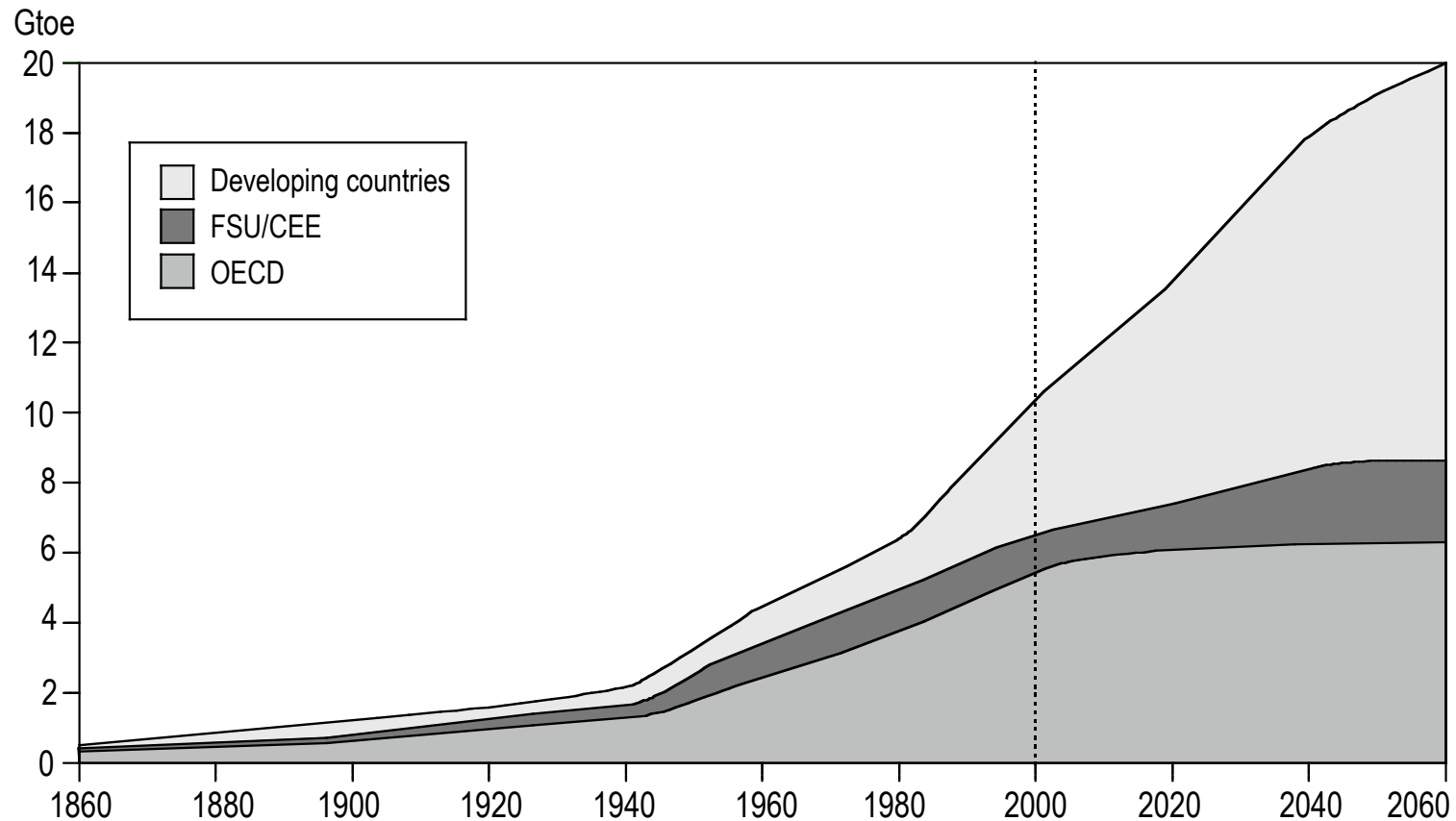
Summary:

- ❑ Continued reliance on fossil fuels demands that effective, safe, and practical CO₂ capture/storage technologies be found and deployed.
- ❑ The current emphasis on molecular CO₂ capture and storage is economically and environmentally risky.
- ❑ Chemistry-based approaches to CO₂ sequestration are desirable because they can:
 - Eliminate capture/pressurization costs
 - Reduce storage/leakage/safety problems
 - Generate useful byproducts
 - Be very cost-competitive

Projected concentrations of CO₂ during the 21st century are two to four times the pre-industrial level



Increasing CO₂ Driven by Increasing Energy Demand:

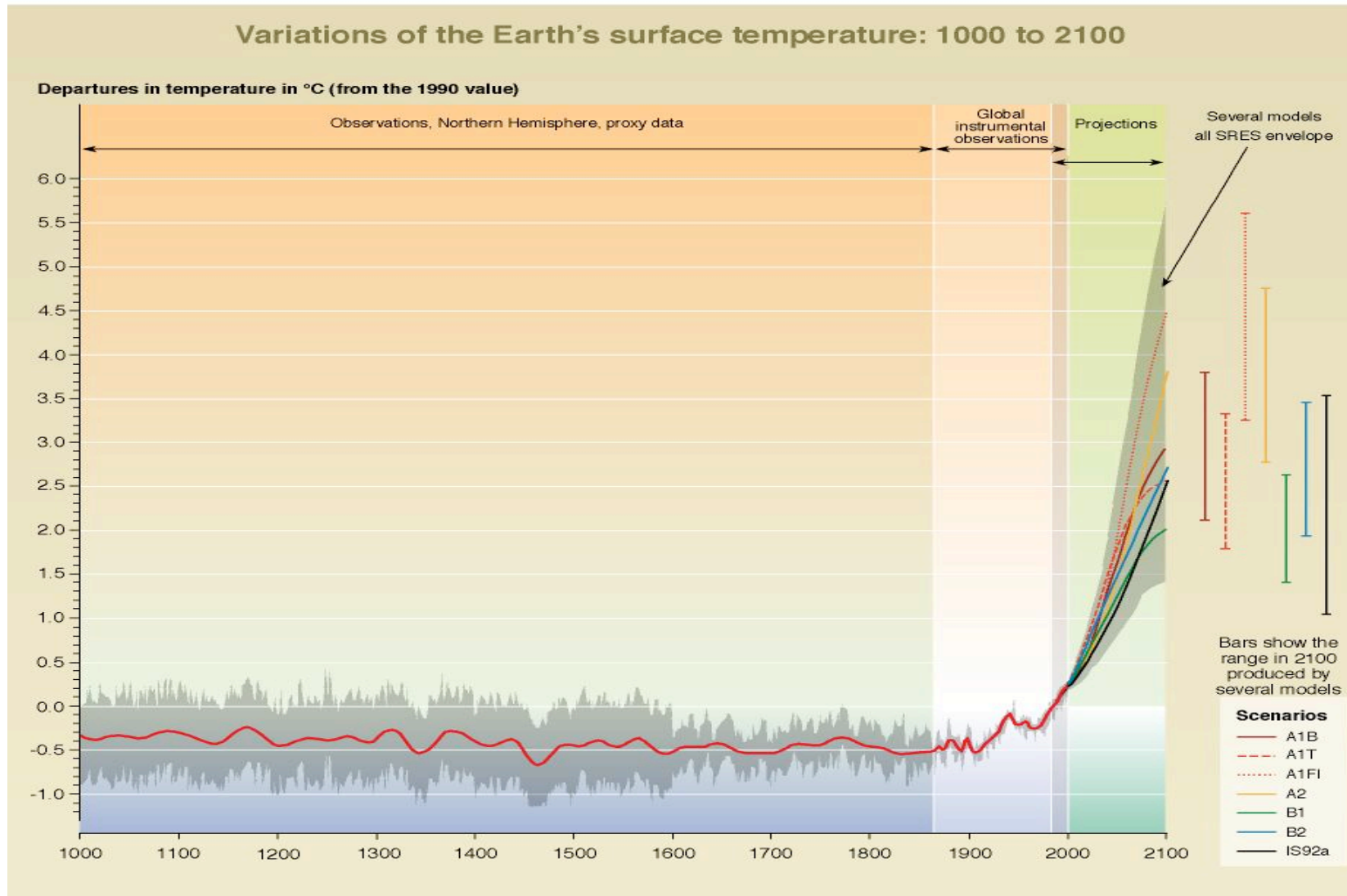


Source: World Energy Council, World Bank.

The graph for the period 2000–2060 shows a scenario of future energy consumption based on current trends.

Projected Temperatures During the 21st Century Are Significantly Higher Than at Any Time During the Last 1000 Years

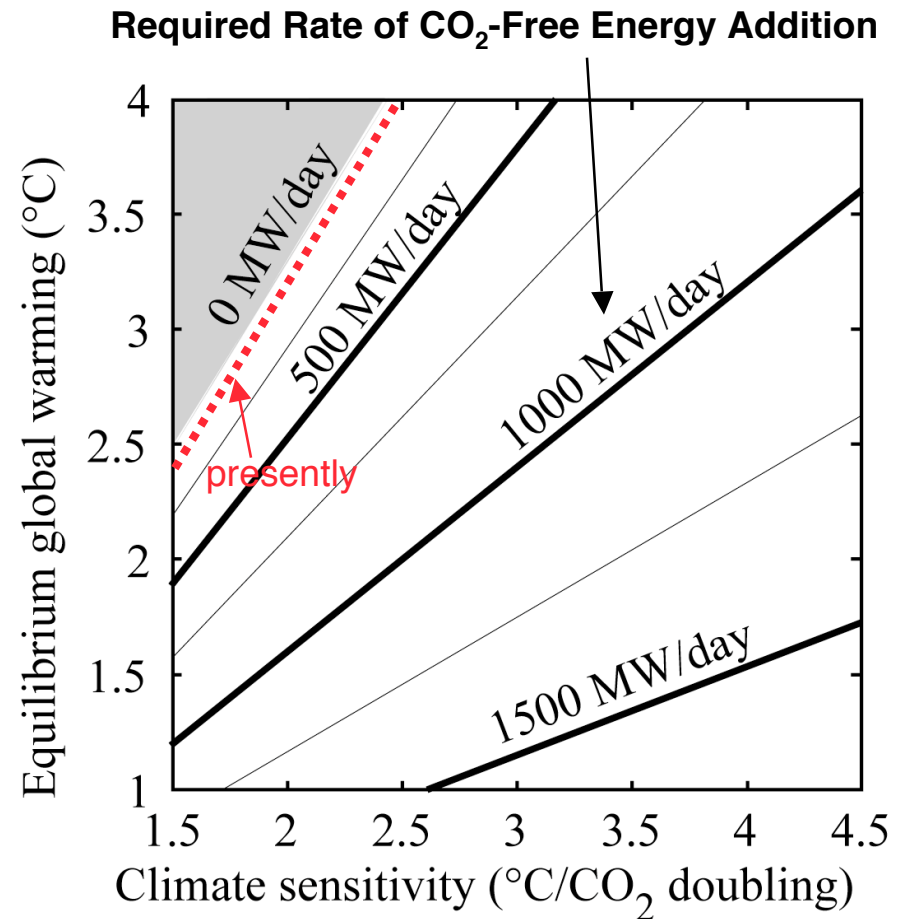
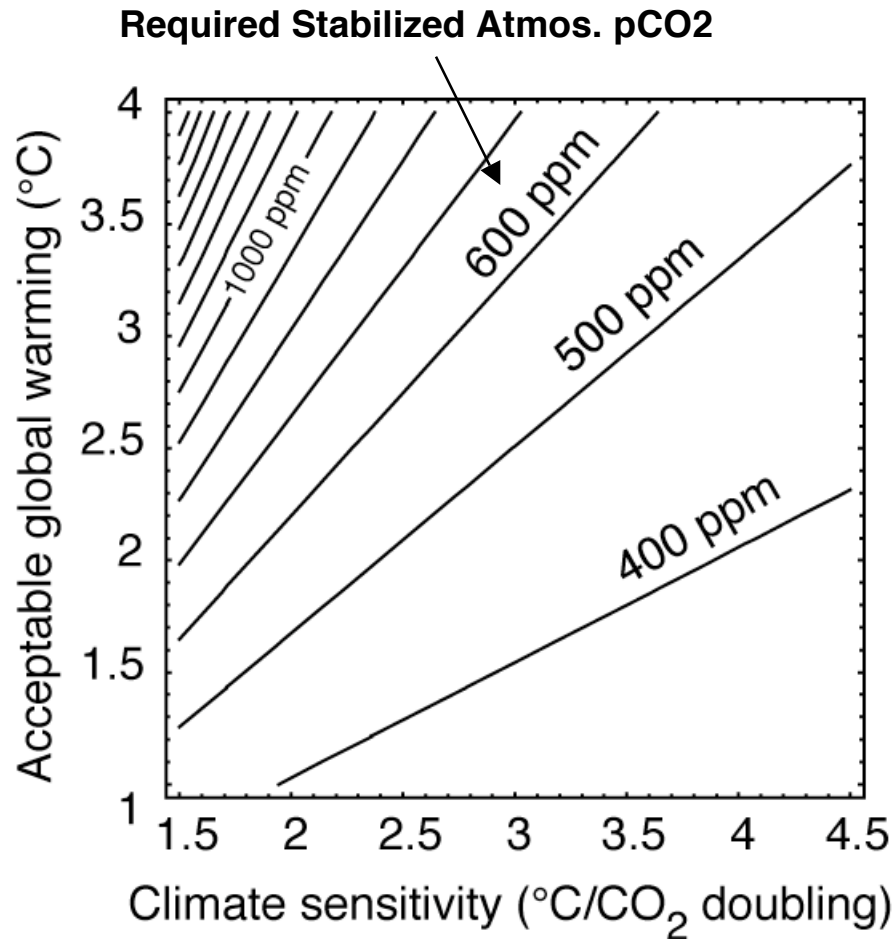
(from IPCC website)



UN Framework Convention on Climate Change

- Signed June 12, 1992
 - by President Bush in Rio de Janeiro, Brazil
- Ratified Oct 15, 1992
 - by the U.S. Senate
- Calls for—
 - “stabilization of greenhouse gases at a level that will prevent dangerous interference with the climate system”
 - “within a time-frame sufficient to allow ecosystems to adapt naturally to climate change”

50-yr Projected pCO₂ and CO₂-Free Energy Requirements for Various Climate Sensitivities and Global Warmings:



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

To add 1 GW_t of 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 inexpensive CO₂ sequestration is essential.**



Another CO₂ Effect:

Ocean chemistry and biology effects -

Air-to-sea diffusion of CO₂ into seawater:



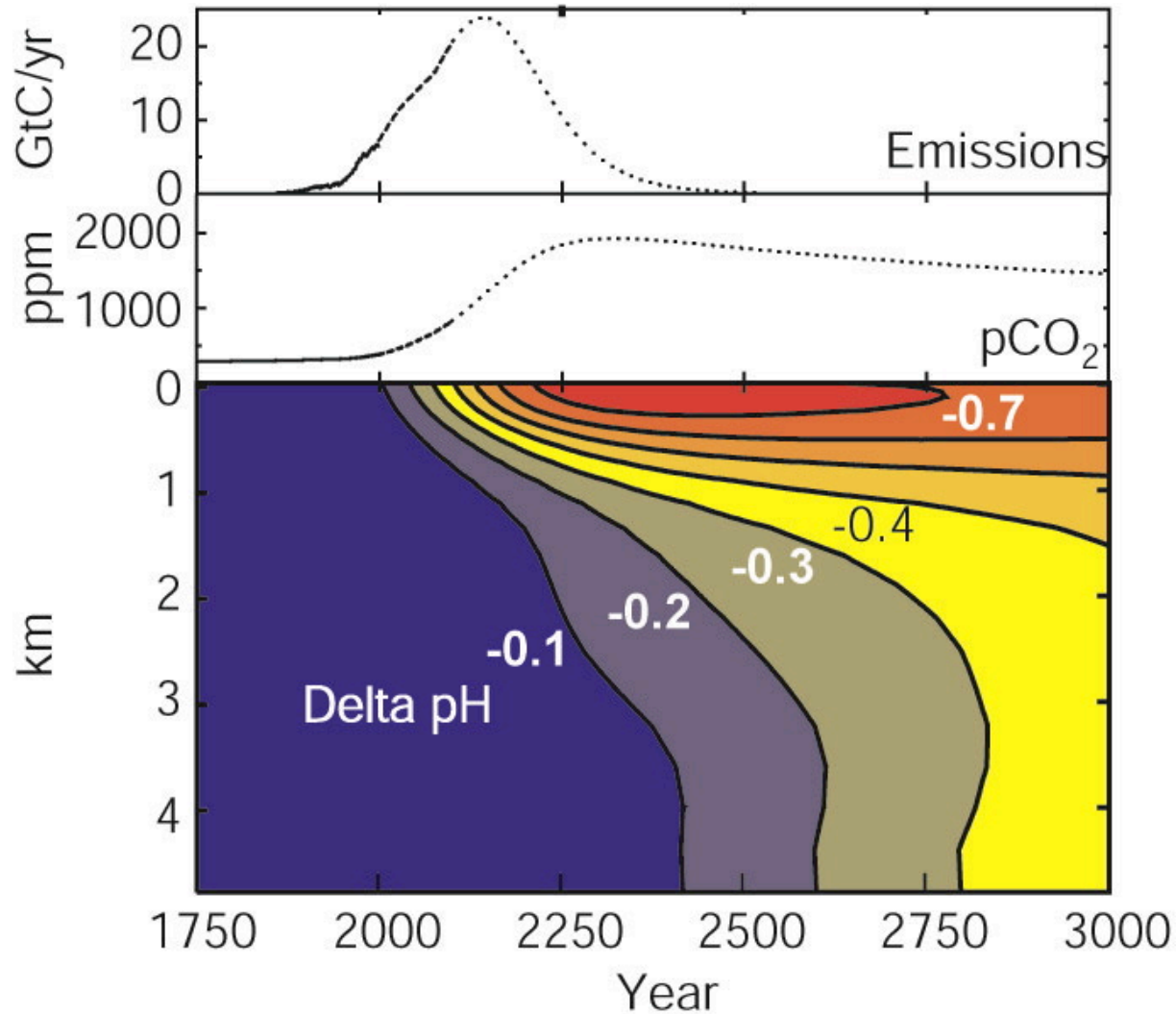
Fate of CO₂ added: (+ 9 %) (+151 %) (– 60%)

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⁺.

Implications for Ocean pH:



(Caldeira and Wickett, 2003, *Nature*
415:265)

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-

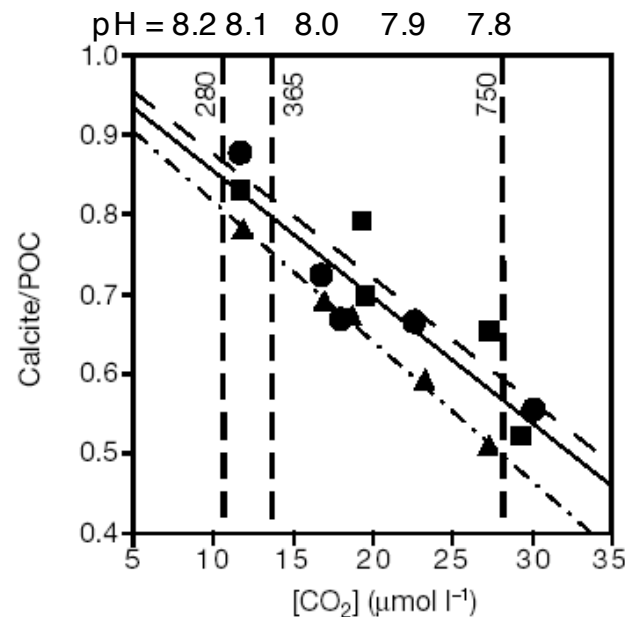


Figure 2 Ratio of calcification to POC production (calcite/POC) of *Emiliania huxleyi* as a function of CO₂ concentration, [CO₂]. Cells were incubated at photon flux densities of 30, 80 and 150 μmol m⁻² s⁻¹ (denoted by circles, squares and triangles and corresponding solid, dashed, dash-dotted regression lines, respectively). Bars denote ± 1 s.d. ($n = 3$); lines represent linear regressions. Vertical lines indicate pCO₂ values of 280, 365 and 750 p.p.m.v.

So climate AND ocean impacts demand that CO₂ emissions be reduced

Possible approaches -

- Increase efficiency of fossil fuel use
- Increase use of non-fossil energy sources
e.g., wind, solar, biomass, nuclear, etc
- Sequestration - active/passive capture and storage
of CO₂ on/in land or ocean**
- (Climate engineering, weather modification, etc)

CO₂ Capture/Sequestration Options:

❑ Land-Based

- Abiotic capture 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

DOE's Goals and Investments:

- ❑ DOE's CO₂ mitigation cost targets:
 - \$2.73/tonne CO₂ for non-point-source methods,
 - “< 10% increase in the cost of energy services for direct capture and sequestration” = <\$5/tonne CO₂

- ❑ Investment in research:
 - \$140M/yr (including non-federal matching)
 - >85% invested in abiotic CO₂ capture with gas or liquid CO₂ storage underground

What's wrong with this picture?:

- ❑ Investment too small given the risks from CO₂ increase
- ❑ Heavy emphasis on molecular CO₂ sequestration assumes this technology will be the primary solution despite the fact that:
 - CO₂ capture and pressurization alone costs >\$30/tonne CO₂
 - Infrastructure for CO₂ transport is largely non-existent
.....requires huge, costly investment in pipelines and wells
 - Ability of underground structures to contain CO₂ remains to be demonstrated

➔ ***Larger investment in a broader range of technologies is needed***

Industry Concerns

“[CO₂] Sequestration is difficult, but if we don't have sequestration then I see very little hope for the world.”

...

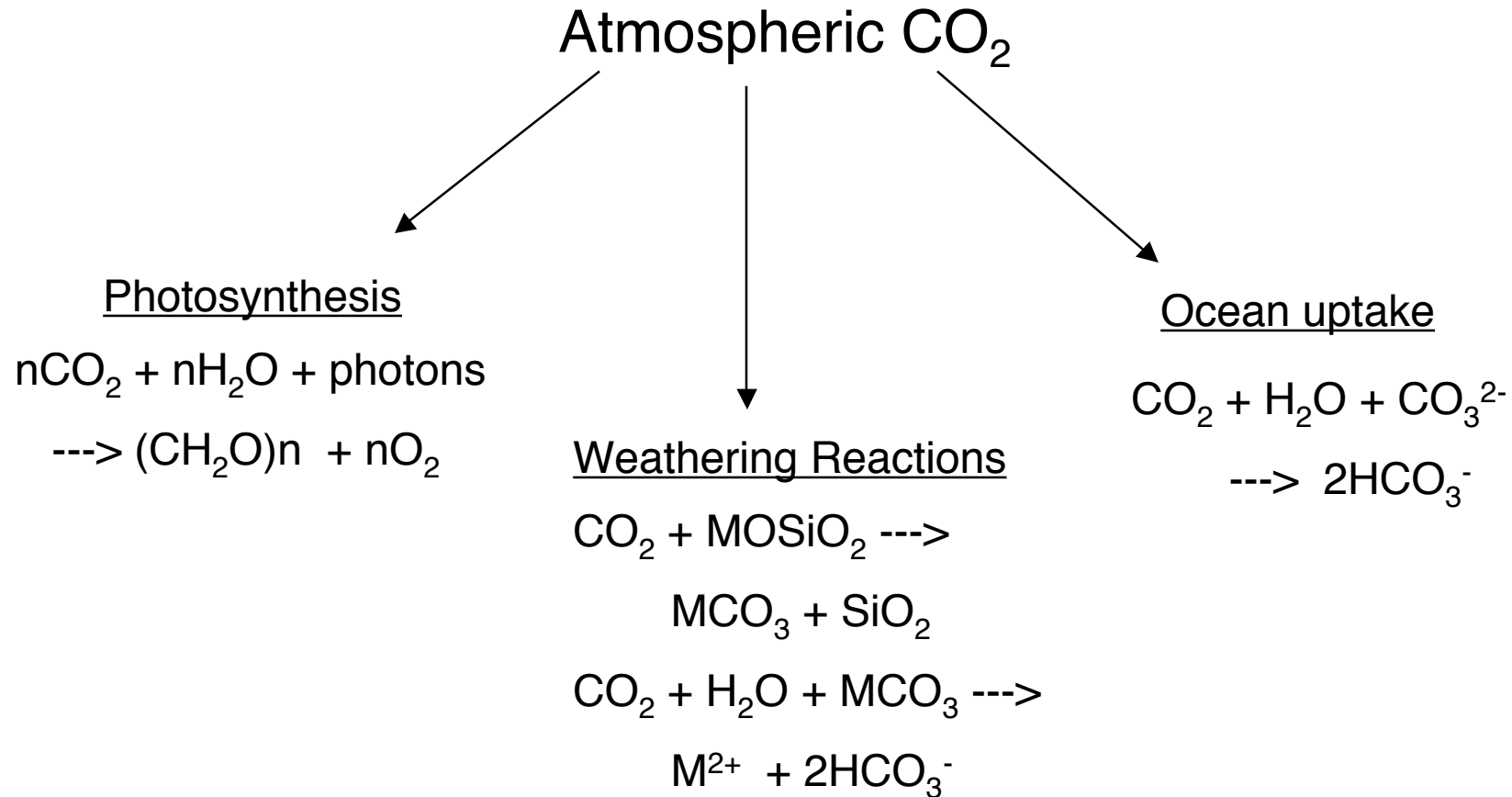
“You probably have to put it [CO₂] under the sea but there are other possibilities. You may be able to trap it in solids or something like that. The timescale might be impossible, in which case I'm really very worried for the planet because I don't see any other approach.”

Lord Ron Oxburgh, Chairman, Shell Oil

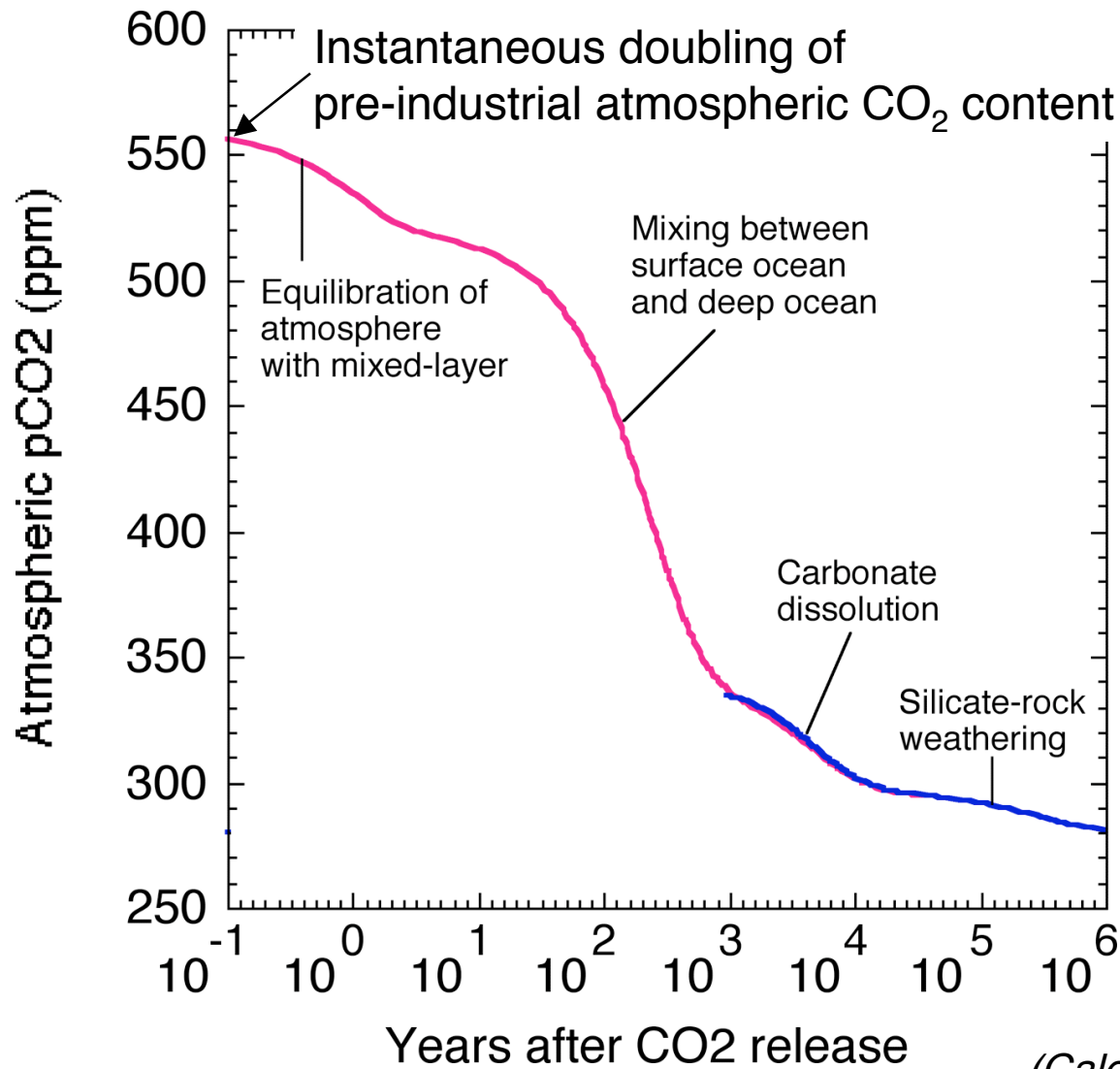
The Guardian, June 17, 2004

Natural Chemical CO₂ Capture and Storage:

Nature's own mechanisms:



Natural CO₂ “capture and sequestration”:



(Caldeira and Rau, 2000)

Weathering Reactions:

Conversion of CO₂ to carbonates:

□ Silicate weathering:

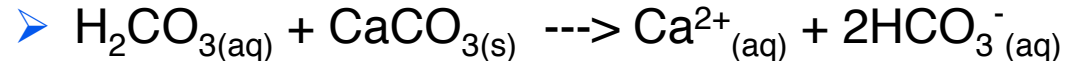
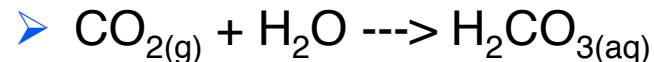


$\Delta G = -20 \text{ to } -65 \text{kJ/mole}$

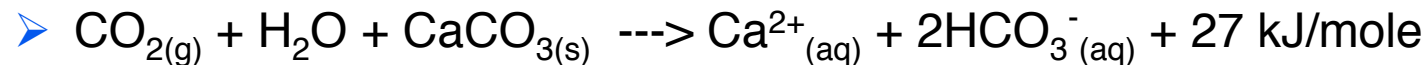
X= divalent metal, e.g., Mg in silicate minerals

(e.g., Lackner, *Ann. Rev. Energy Environ.*, 2002)

□ Carbonate (e.g., limestone) weathering:



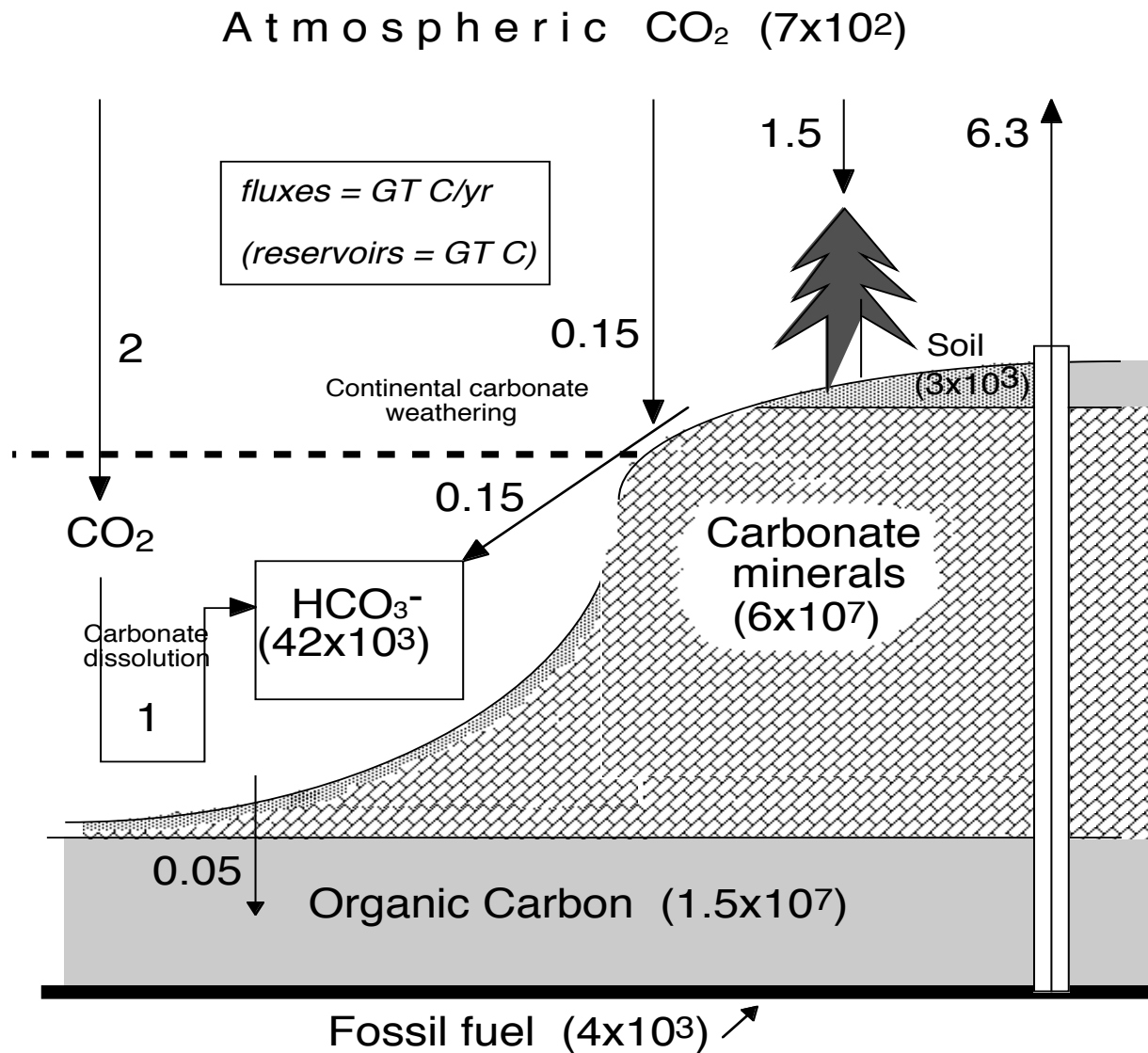
Net reaction:



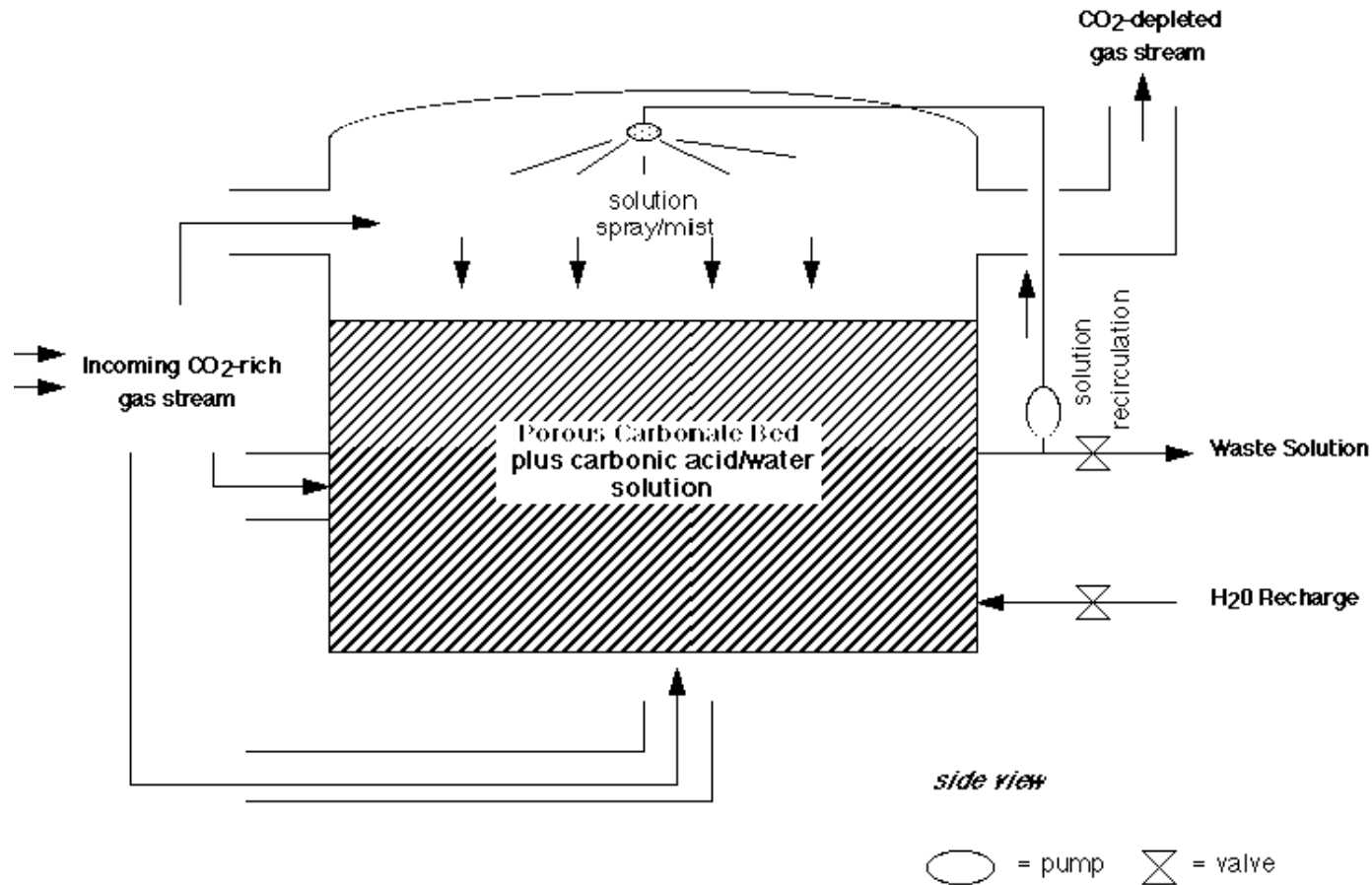
$\Delta G = -12 \text{ kJ/mole}$

(e.g., Rau et al. (1999, 2000, 2002))

Carbonate Weathering in the Global Carbon Cycle:



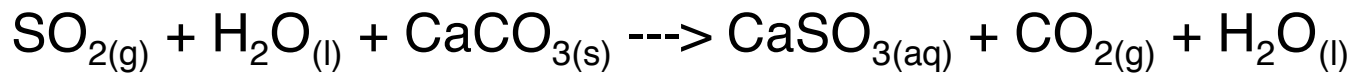
Accelerated Weathering of Limestone (AWL) Reactor:



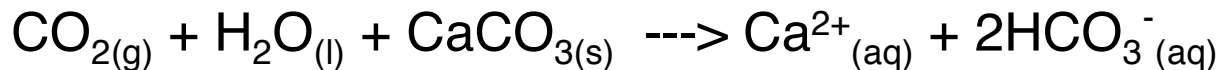
(Rau and Caldeira, 1999)

Analogies to Flue Gas Desulfurization:

FGD:

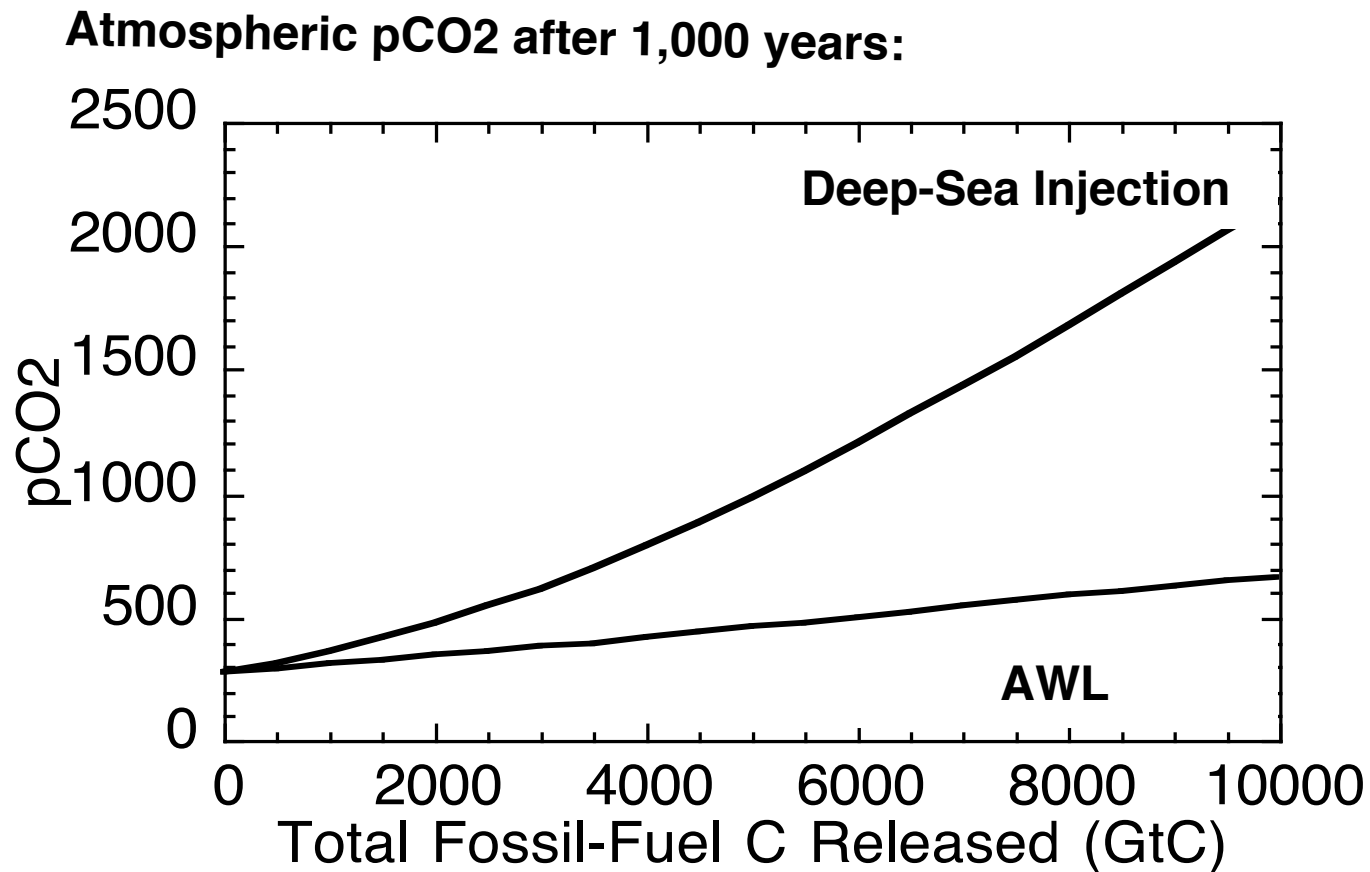


AWL:



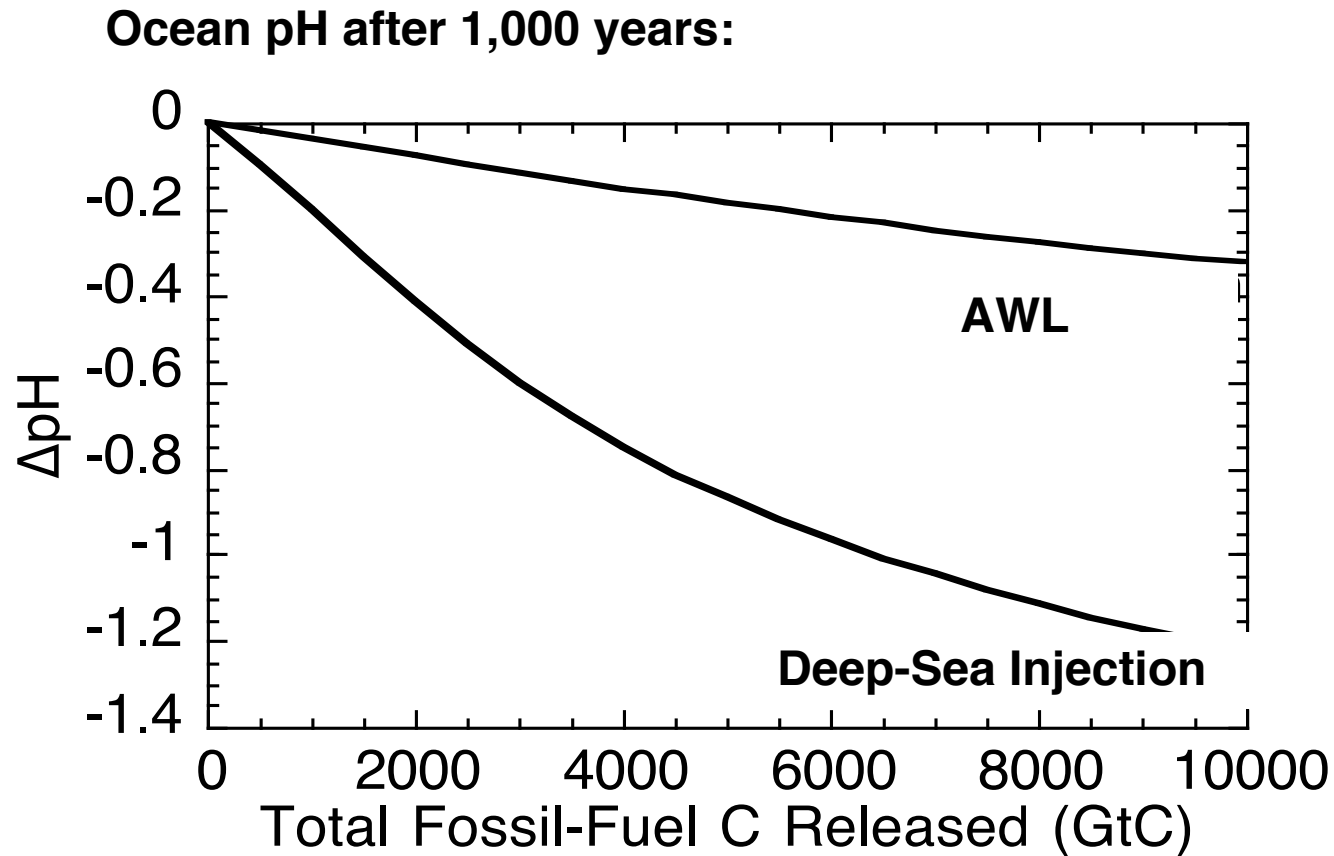
→ Gases captured via reaction with wet limestone (at ambient temperature and pressure), and converted to benign, storable/useable liquids or solids

Direct 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 -

- ◆ 10⁴ m³, pumped 2 vertical meters = \$ 7.57

➤ Capital and maintenance = \$ 2.50

TOTAL:

\$ 29/tonne CO₂

Optimum 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 -

- ◆ 10⁴ m³, pumped 2 vertical meters = ~~\$ 7.57~~

➤ Capital and maintenance = \$ 2.50

TOTAL:

<\$5/tonne CO₂

Advantages of AWL:

❑ Abundant and cheap reactants:

- Limestone - carbonates = 6×10^7 Gt C, fossil fuels = 4×10^3 Gt C;
H₂O - ocean = 1.4×10^{18} m³

❑ 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

Possible Negative Impacts/Limitations:

- ❑ Local availability of limestone and water limits application
 - could be offset by piping CO₂ to favorable reactor sites
 - use inland water co-produced with oil?
- ❑ Biological impacts -
 - need to consider pre-dilution effluent effects
 - trace contaminants from flue gas or limestone?
- ❑ Environmental and economic impacts due to increased limestone mining/transport

Accelerated Weathering of Limestone Summary:

□ Accelerated limestone weathering may have significant advantages over other forms of point-source CO₂ mitigation, especially where limestone and water are readily available.

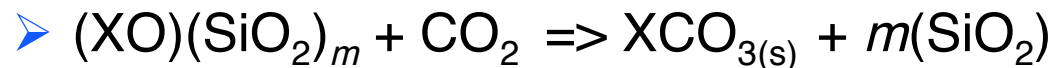


□ This approach deserves to be more fully evaluated as part of the emerging, national and global strategy for CO₂ mitigation.

Geochemical Weathering Reactions:

Conversion of CO₂ to carbonates (carbonation):

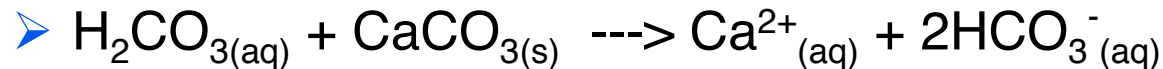
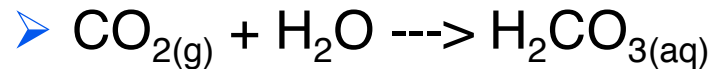
□ Silicate weathering:



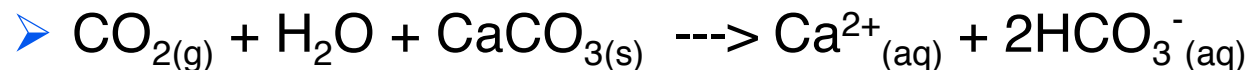
X= divalent metal, e.g., Mg in silicate minerals

(e.g., Lackner, *Ann. Rev. Energy Environ.*, 2002)

□ Carbonate (e.g., limestone) weathering:



Net reaction:



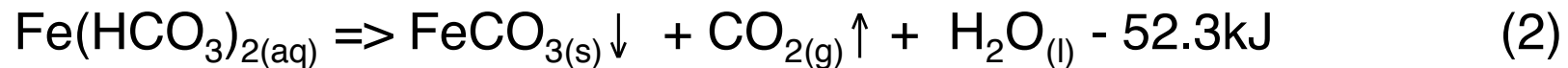
(e.g., Rau et al. (1999, 2000, 2002))

Why Not Form Iron Carbonates?:

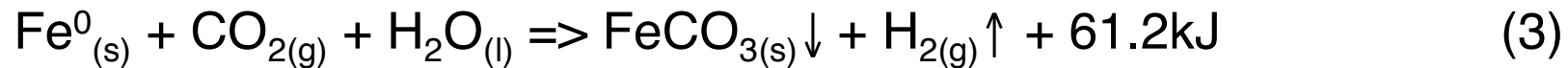
From corrosion science:



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



Net reaction:

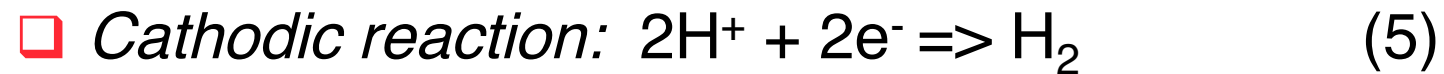
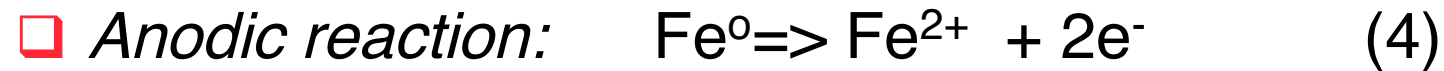


$$\text{DG} = -35.2\text{kJ @ } 25^\circ\text{C}$$

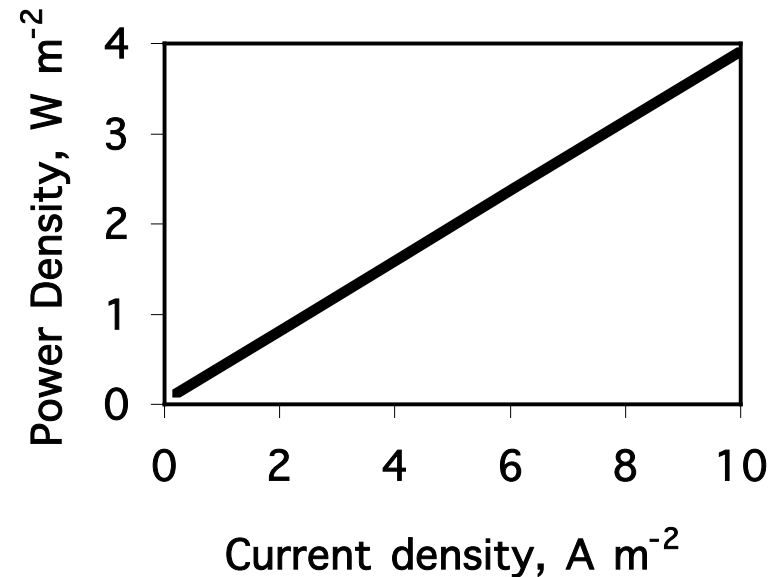
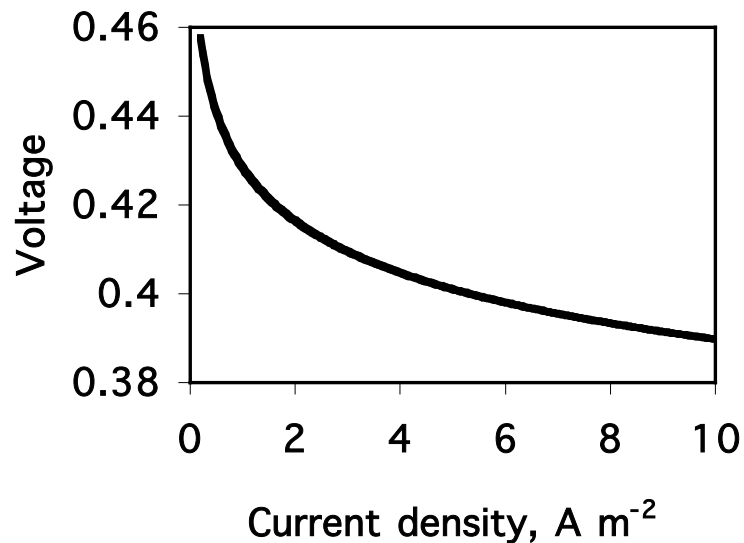
Thus, at ambient temperature and pressure:

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

Electricity Generation - an Fe/CO₂ Galvanic Cell:

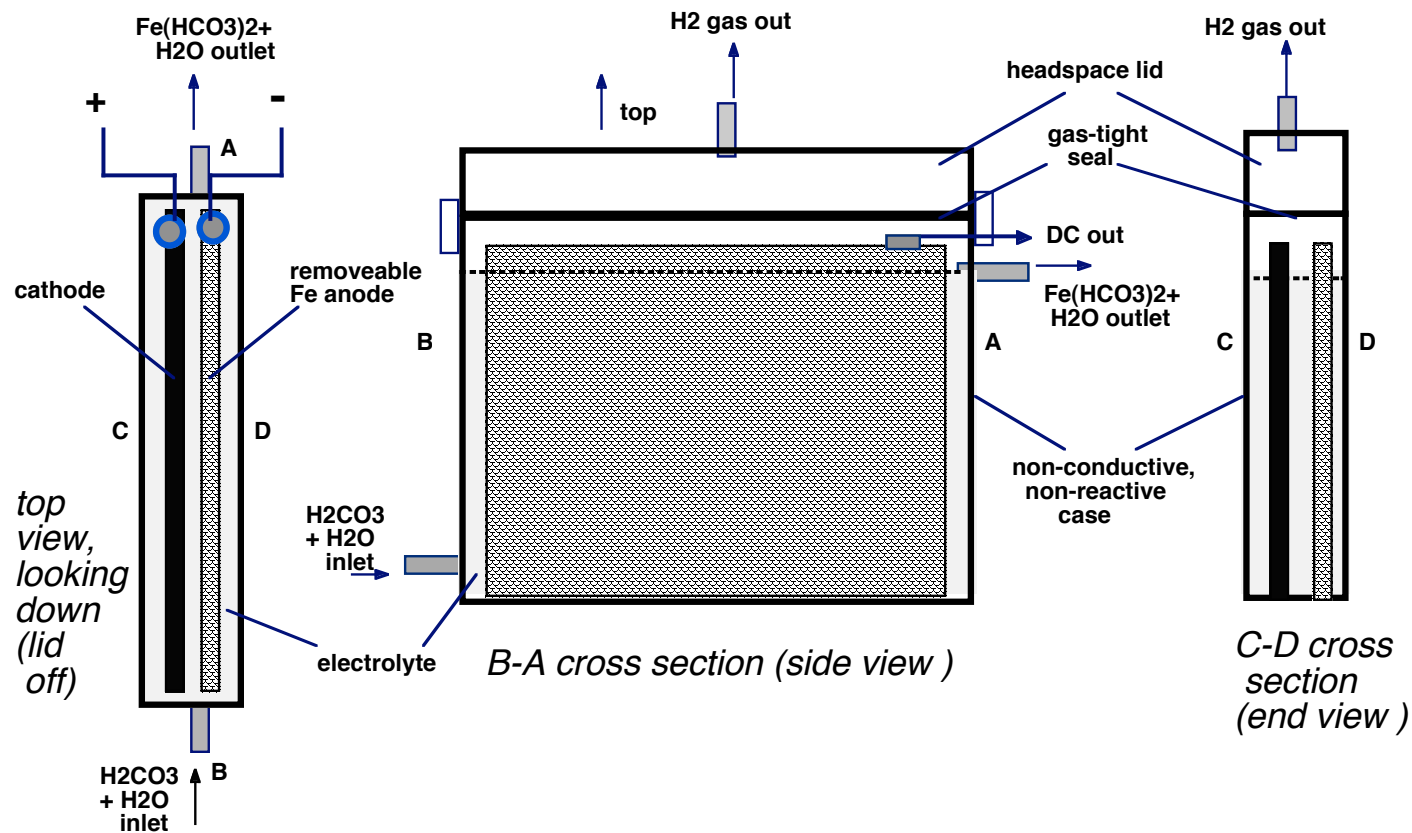


e.g., from Hasenberg (1988):

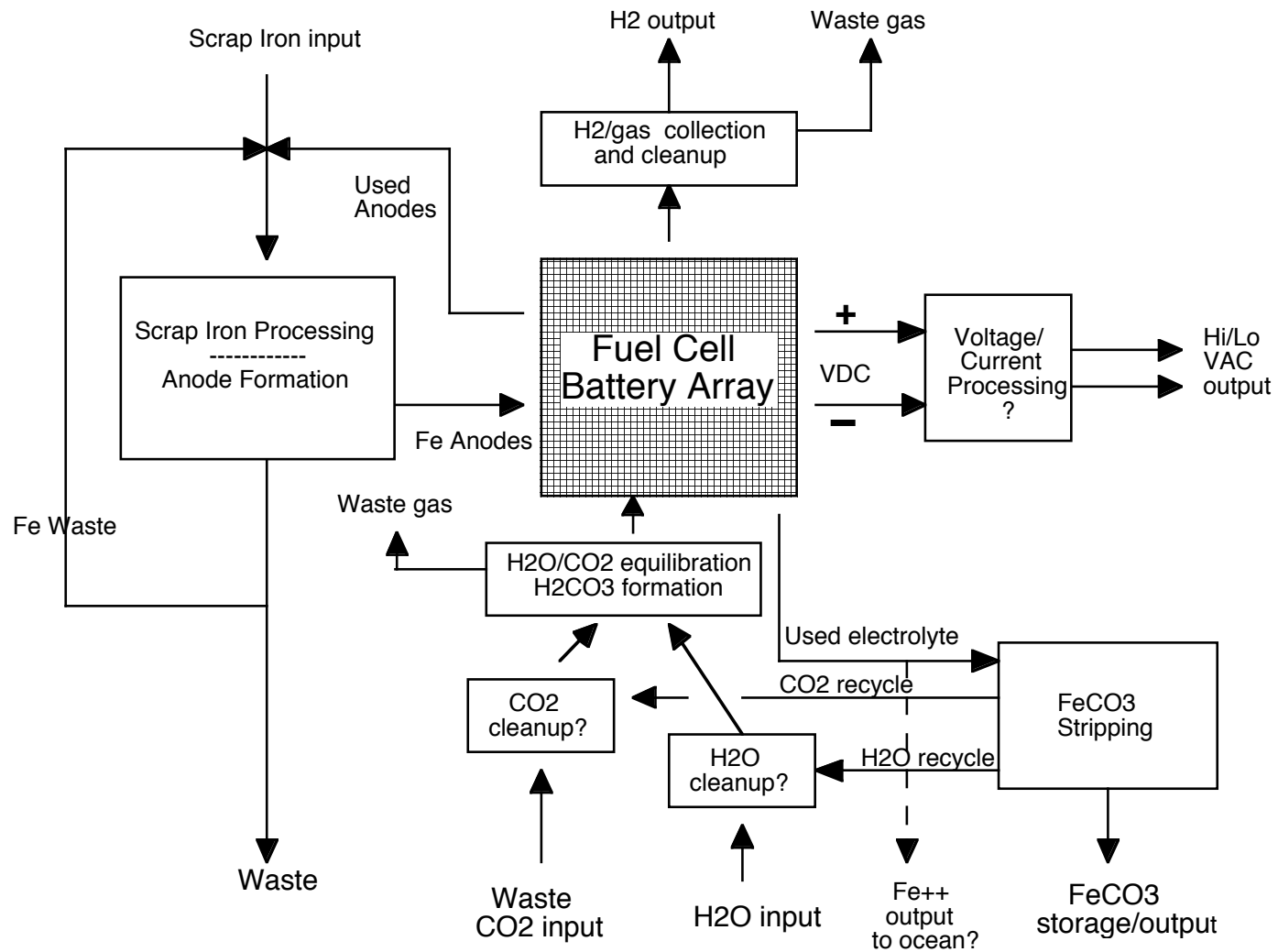


Possible Fe/CO₂ Fuel Cell Design:

Example of Fe/CO₂ Fuel Cell:



Large-Scale Fe/CO₂ Fuel Cell Operation:



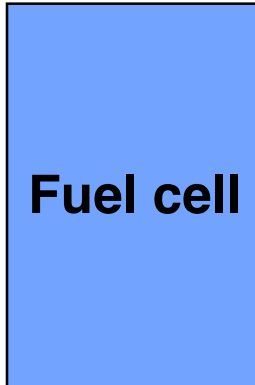
Fe/CO₂ Fuel Cell Requirements/Yields:

Mass in (tonnes):

1 Fe⁰ -->

0.79 CO₂ -->

0.32 H₂O -->



Mass/energy out:

--> 2.07 FeCO₃

--> 0.04 H₂

--> 421kWh_e(tonne⁻¹ Fe hr⁻¹)

CO₂ Mitigation Implications:

Fe/CO₂ fuel cells would consume CO₂ per tonne Fe:

- 0.8 tonnes CO₂ (forming FeCO₃) or
- 1.6 tonnes CO₂ (forming Fe(HCO₃)₂)
- Plus avoid: 0.3 tonnes CO₂ in H₂ production; 0.4 tonnes electric. prodctn.

So Fe in fuel cells would mitigate 1.5 to 2.3 tonnes CO₂/tonne Fe

Capacity:

Thus, using 10⁸ tonnes/yr of scap iron in Fe/CO₂ fuel cells could:

mitigate 1.5 to 2.3x10⁸ tonnes CO₂/yr (6-10% of CO₂ from US electricity production)

while:

producing 3.6x10⁶ tonnes H₂ (40% of US H₂ production) and

producing 4.2x10¹⁰ kWh_e (<1% US generation)

Fe Sources and CO₂ Sequestration Implications:

CO₂ generation per tonne new iron metal produced:

(from Anderson et al., Mitrex Technologies Inc.)

- from scrap - 0.4 tonnes CO₂ (all smelting methods)
- from iron ore - 1.3 tonnes CO₂ (EAF), 1.7 tonnes CO₂ (BF)

Therefore, recycling scrap iron to produce new iron metal

avoids 0.9 - 1.3 tonnes CO₂/tonne Fe

In contrast, scrap iron use in Fe/CO₂ fuel cells

mitigates 1.5 - 2.3 tonnes CO₂/tonne Fe

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 -

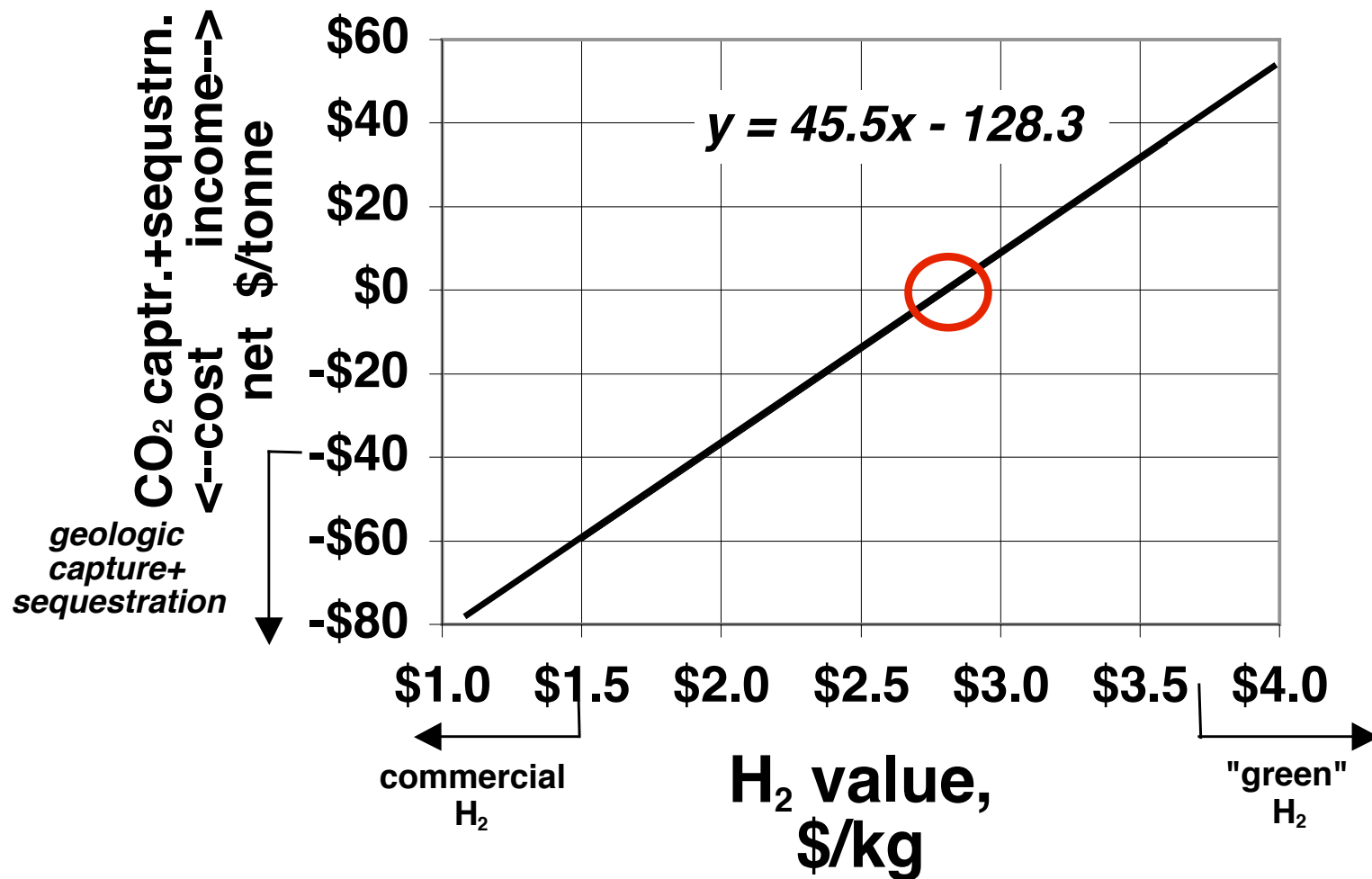
FeCO₃ = \$3.80/tonne

H₂ = \$2,800/tonne (\$2.80/kg)

Electricity = \$0.05/kWh_e

Overhead = \$50.00/tonne Fe reacted

Fuel Cell Net Cost or Profit?



Fe/CO₂ Fuel Cell Feature Summary:

- ❑ CO₂ captured and sequestered as dissolved or solid iron carbonate at ambient temperature and pressure.
- ❑ Carbon-free, “green” hydrogen and electricity are produced.
- ❑ The value of the hydrogen and electricity produced will offset the cost of CO₂ mitigation (or make it profitable?), depending on market and regulatory conditions.
- ❑ Potentially can be retrofitted to any CO₂ waste stream
 - separate, costly CO₂ capture step avoided
 - gasification/reforming or IGCC turbine flue gas particularly attractive ...concentrated CO₂ stream means high fuel cell reaction densities; augments existing H₂/electricity infrastructure and production

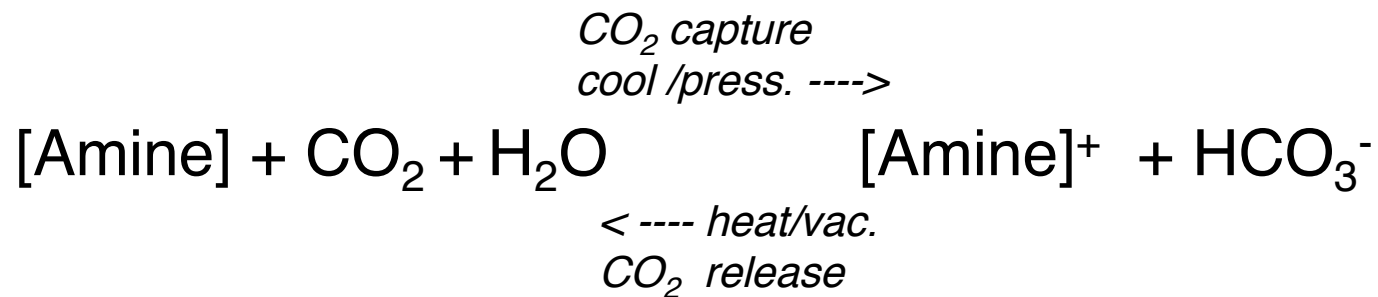
Fe/CO₂ Fuel Cell Caveats/Limitations:

- ❑ Because of the cost and carbon intensity of new iron and steel production, best Fe source for fuel cells would be “stranded” scrap metal not already being recycled.
- ❑ CO₂ mitigation capacity may therefore limited by scrap iron availability

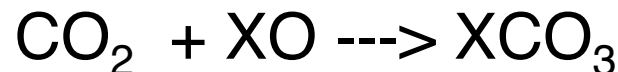
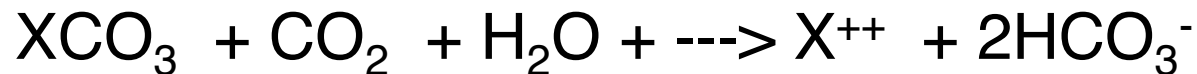
(However, sequestering CO₂ as Fe(HCO₃)₂ rather than as FeCO₃ doubles the sequestration potential per tonne Fe. Further, using Fe(HCO₃)₂ to enhance photosynthesis in the ocean would probably increase the sequestration potential by >10⁴X)
- ❑ The economics of Fe/CO₂ fuel cells is highly dependent on the market value of scrap iron, hydrogen, electricity, and the CO₂ mitigated, as well as the capital, operating, and maintenance costs of the system.

Chemistry in Geologic CO₂ Storage:

- ❑ Chemistry is essential to current CO₂ capture technologies.
e.g. amine capture:



- ❑ Post-injection chemical reactions increases effectiveness and safety of underground CO₂ storage, i.e., “ionic and mineral trapping” :



General Conclusions:

- ❑ CO₂ mitigation presents a major societal and technological challenge.
- ❑ Practical, inexpensive, and safe ways of capturing and sequestering CO₂ are needed.
- ❑ ***Chemical CO₂ sequestration options have some attractive advantages and need to be seriously evaluated in parallel with other technologies.***
- ❑ ***Partners and funding needed.***

Further Information:

- **Rau, G.H. and K. Caldeira.** 1999. Enhanced carbonate dissolution: A means of sequestering waste CO₂ as ocean bicarbonate. ***Energy Conversion and Management*** 40: 1803-1813.
- **Caldeira, K. and G.H. Rau.** 2000. Accelerating carbonate dissolution to sequester carbon dioxide in the ocean: Geochemical implications. ***Geophysical Research Letters*** 27: 225-228.
- **Rau, G.H. and K. Caldeira.** 2002. Minimizing effects of CO₂ storage in the oceans. ***Science*** 295:275-276.
- **Rau, G.H.** 2004. Possible use of Fe/CO₂ fuel cells for CO₂ mitigation plus H₂ and electricity production. ***Energy Conversion and Management*** 45: 2143-2152.
- **Rau, G.H., K.G. Knauss, W. Langer, K. Caldeira.** Reducing energy-related CO₂ emissions using accelerated limestone weathering. ***Energy*** (submitted)

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