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

GCEP/Stanford April 15, 2008

Overview

- ❑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.:

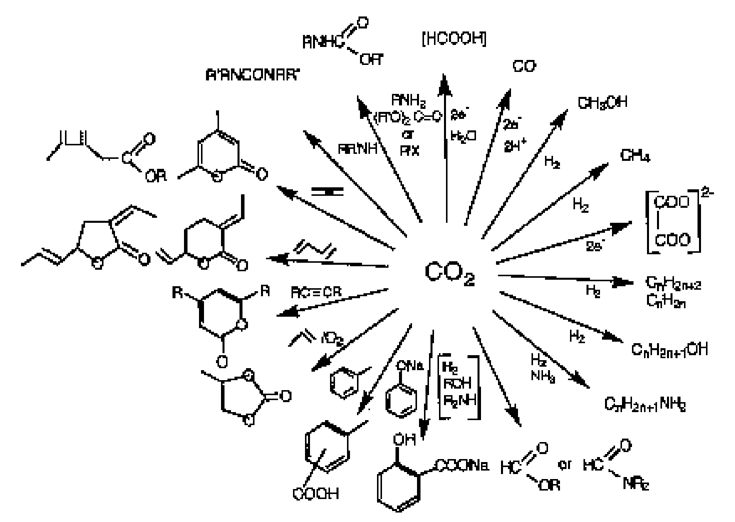
CO_2

$+ \ OH^- \text{ ----> } HCO_3^-$

$+ \ CO_3^{2-} + H_2O \text{ ---->} 2HCO_3^-$

$+ \ MO \text{ ----> } MCO_3$

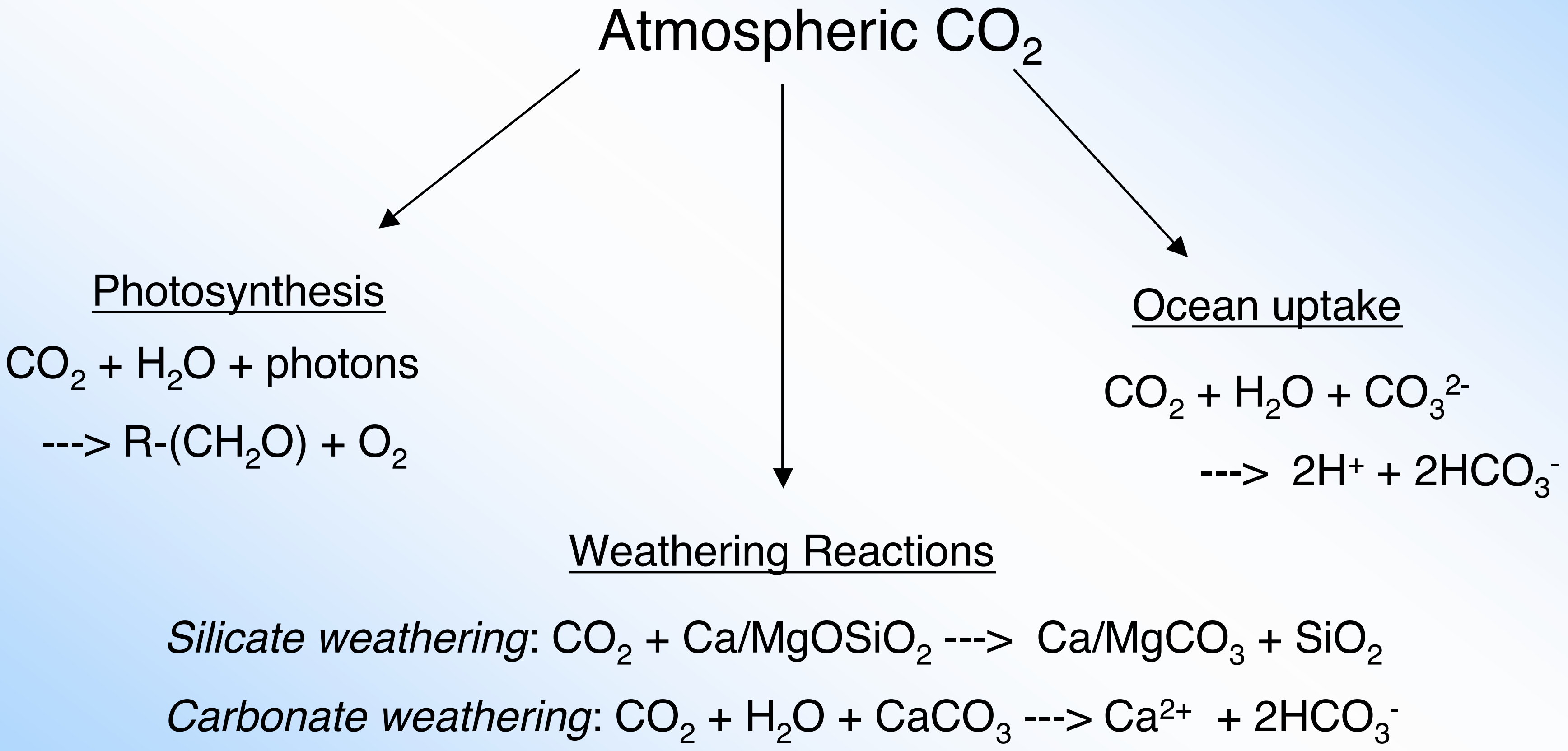
$+ \ M^0 + H_2O \text{ ----> } MCO_3 + H_2$



- 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

$CO_2 + H_2O$ + photons

---> $R\text{-}(CH_2O) + O_2$

Ocean uptake

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

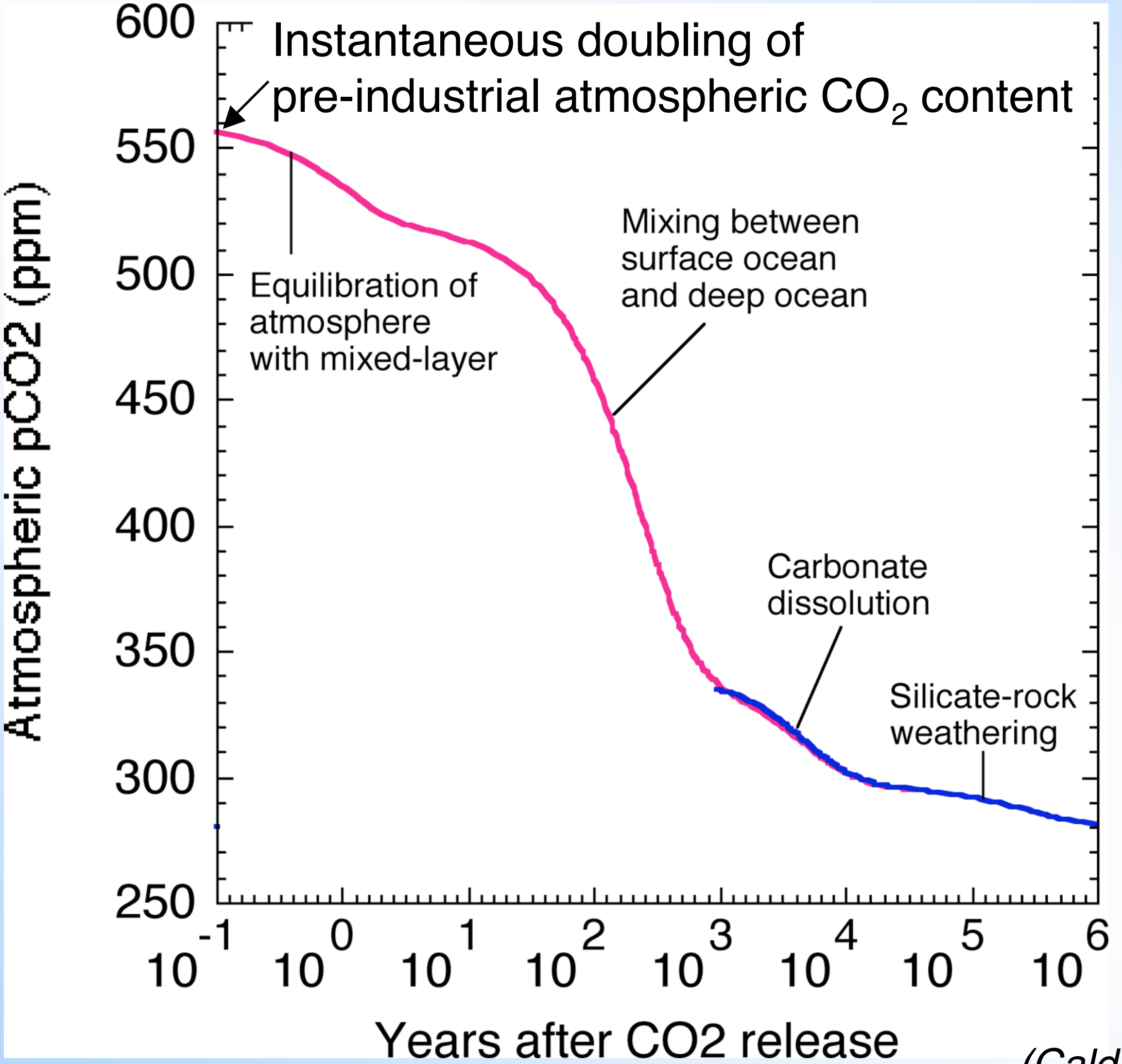
---> $2H^+ + 2HCO_3^-$

Weathering Reactions

Silicate weathering: CO_2 + Ca/$MgOSiO_2$ ---> Ca/$MgCO_3 + SiO_2$

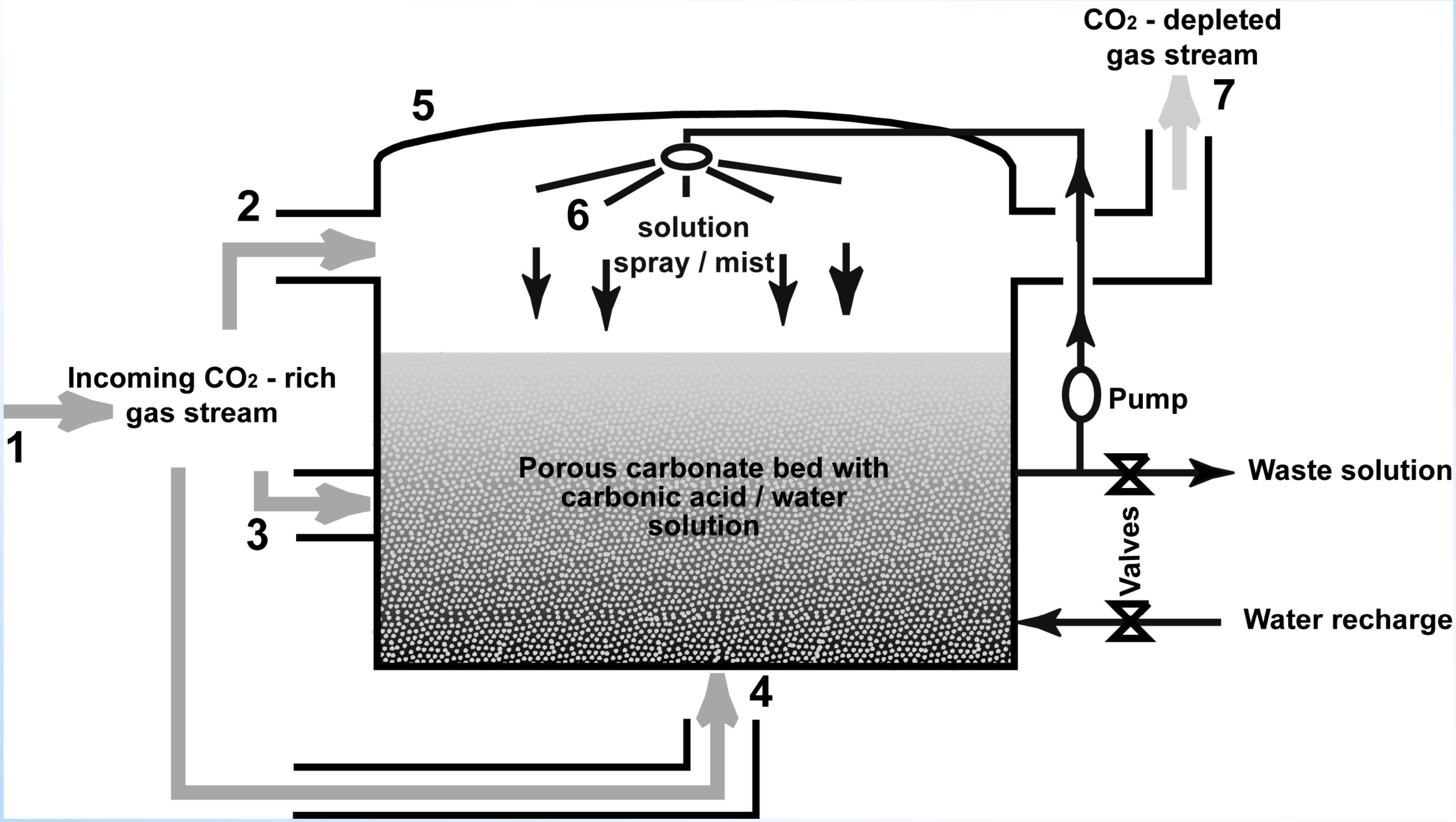
Carbonate weathering: $CO_2 + H_2O + CaCO_3$ ---> $Ca^{2+} + 2HCO_3^-$

Natural CO_2 Sequestration: Effective but slow



(Caldeira and Rau, 2000)

Accelerated Weathering of Limestone (AWL) Reactor:



(Rau and Caldeira, 1999)

Analogies to Flue Gas Desulfurization:

AWL:

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

FGD:

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

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

→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_2 avoided

CO_2 Mitigation In Cement Manufacture:

CCAP Report 2005: CA Cement Manufacture -

- Current state emissions ≈ 10.5 MMT CO_2/yr
  - Flue gas is 20-30% CO_2
- Est. BAU emissions in 2020 = 13.6 MMTCO_2/yr
- Might be reduced to 11 MMTCO_2/yr by 2020 at a cost <$10/tonne CO_2 via:
  - Limestone or flyash + cement blends
  - Alternative fuels
- But AB 32 mandates state return to 1990 emissions (CA cement, est. 7.8 MMTCO_2/yr) by 2020
- ***Therefore, current CO_2 reduction path inadequate.***

Chemical Composition of CKD:

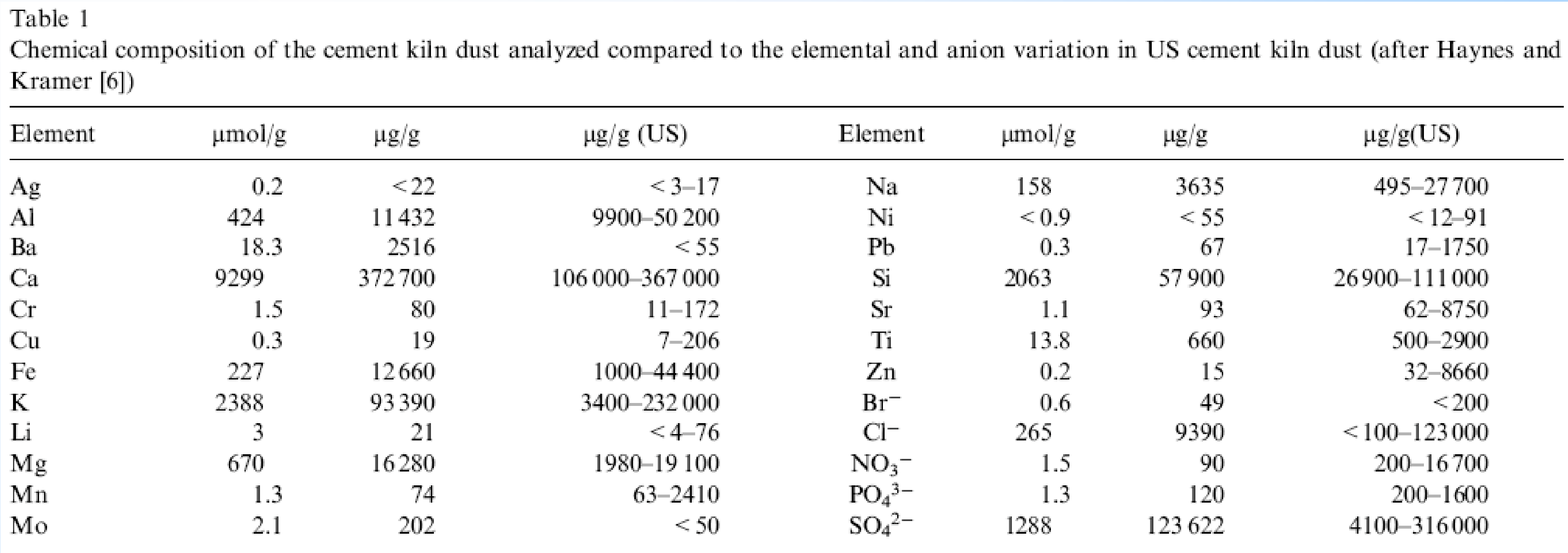


Table 1

Chemical composition of the cement kiln dust analyzed compared to the elemental and anion variation in US cement kiln dust (after Haynes and Kramer [6])

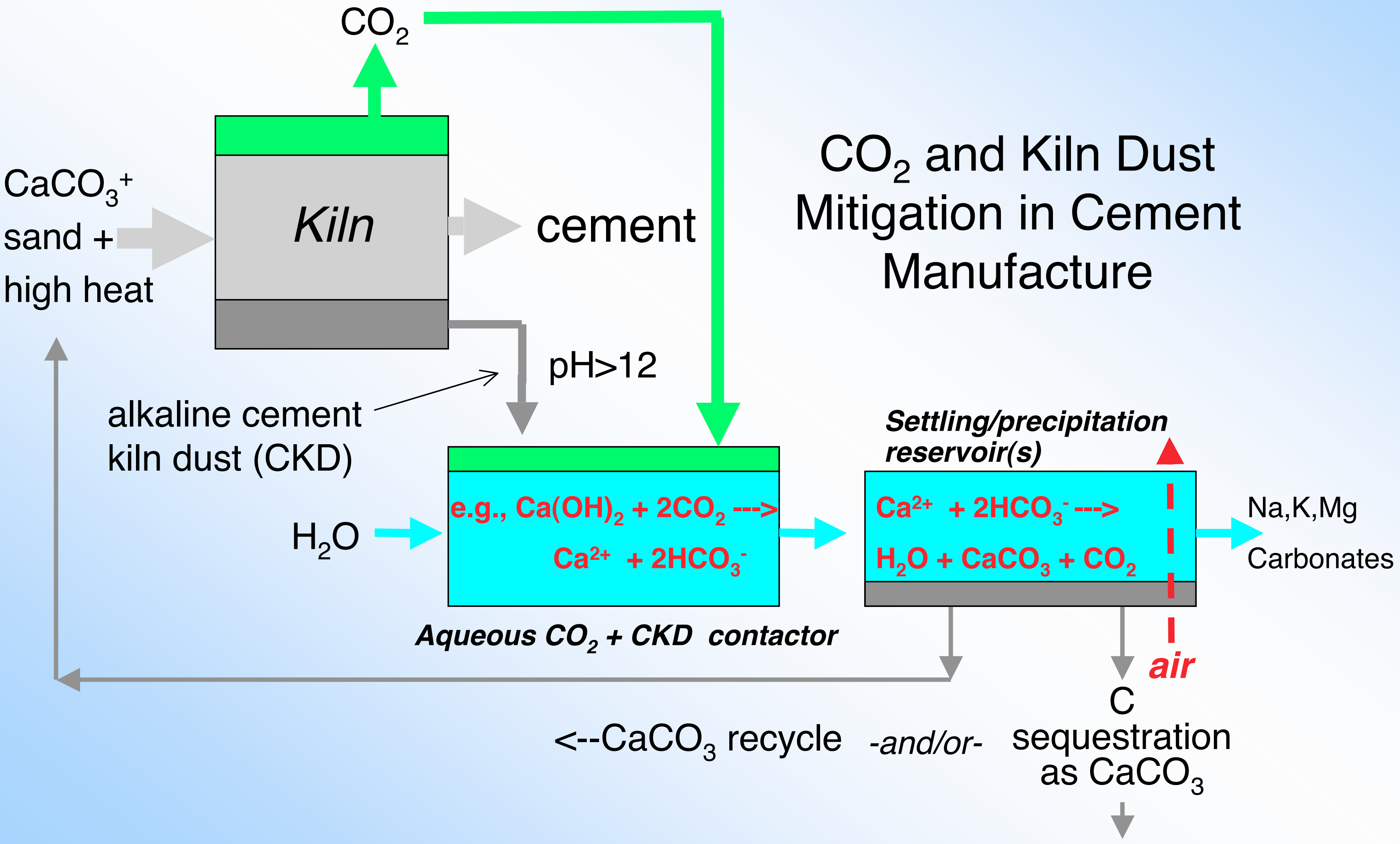
Element	μmol/g	μg/g	μg/g (US)	Element	μmol/g	μg/g	μg/g(US)
Ag	0.2	< 22	< 3–17	Na	158	3635	495–27 700
Al	424	11 432	9900–50 200	Ni	< 0.9	< 55	< 12–91
Ba	18.3	2516	< 55	Pb	0.3	67	17–1750
Ca	9299	372 700	106 000–367 000	Si	2063	57 900	26 900–111 000
Cr	1.5	80	11–172	Sr	1.1	93	62–8750
Cu	0.3	19	7–206	Ti	13.8	660	500–2900
Fe	227	12 660	1000–44 400	Zn	0.2	15	32–8660
K	2388	93 390	3400–232 000	Br^-	0.6	49	< 200
Li	3	21	< 4–76	Cl^-	265	9390	< 100–123 000
Mg	670	16 280	1980–19 100	NO_3^-	1.5	90	200–16 700
Mn	1.3	74	63–2410	PO_4^{3-}	1.3	120	200–1600
Mo	2.1	202	< 50	SO_4^{2-}	1288	123 622	4100–316 000

Duchesne and Reardon, 1998

- Strongly alkaline waste (pH >12); highly reactive with acid gases including CO_2
- 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 CO_2 /T CKD = <u>75 MMT CO_2</u>

Use Highly Alkaline Waste Cement Kiln Dust for CO_2 Mitigation:



CO_2

$CaCO_3$+
sand +
high heat

Kiln

cement

CO_2 and Kiln Dust
Mitigation in Cement
Manufacture

pH>12

alkaline cement
kiln dust (CKD)

H_2O

e.g., $Ca(OH)_2 + 2CO_2 \rightarrow Ca^{2+} + 2HCO_3^-$

Aqueous CO_2 + CKD contactor

Settling/precipitation reservoir(s)

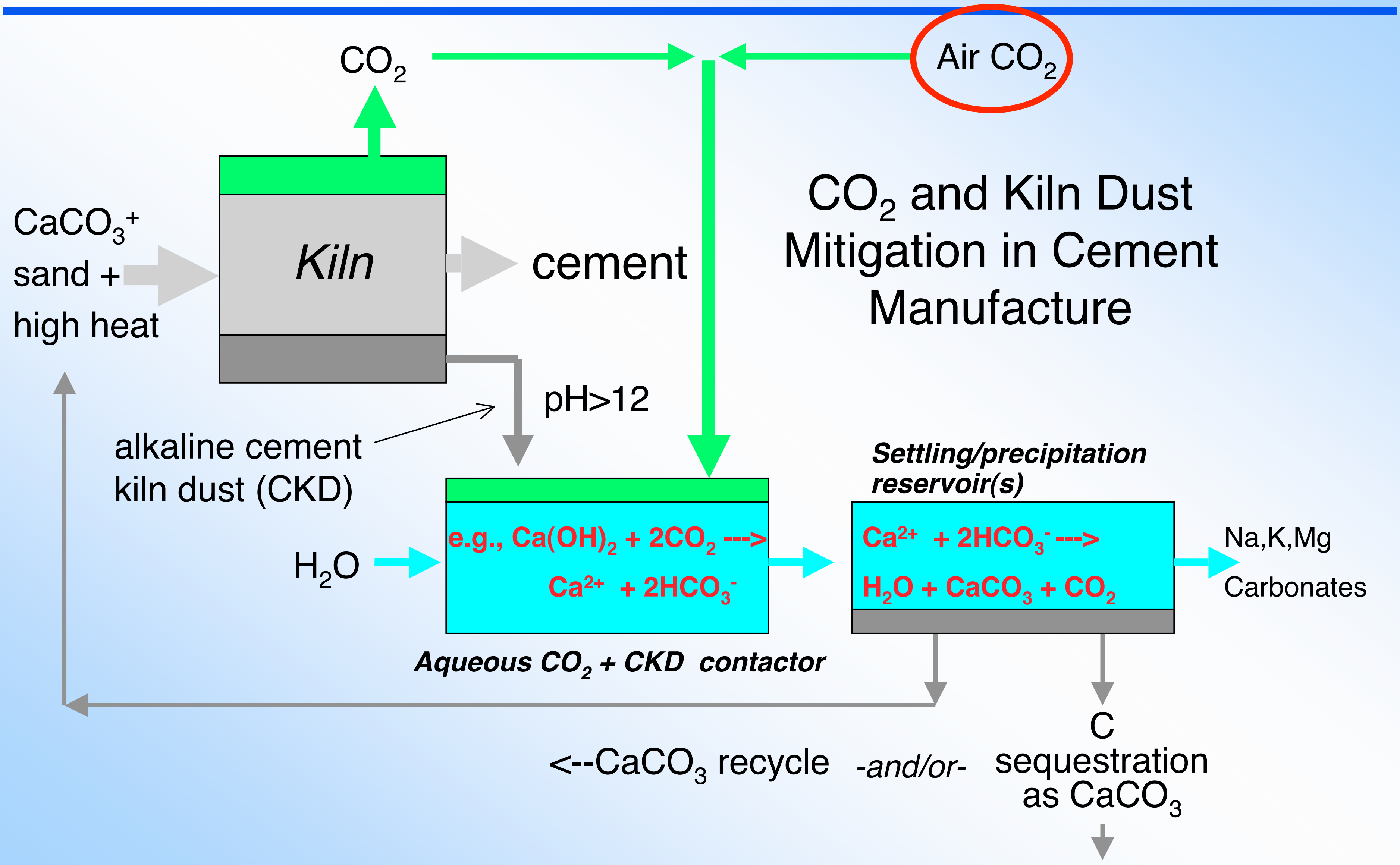
$Ca^{2+} + 2HCO_3^- \rightarrow H_2O + CaCO_3 + CO_2$

air

Na,K,Mg
Carbonates

<--$CaCO_3$ recycle *-and/or-* C sequestration as $CaCO_3$

Air CO_2 capture option:



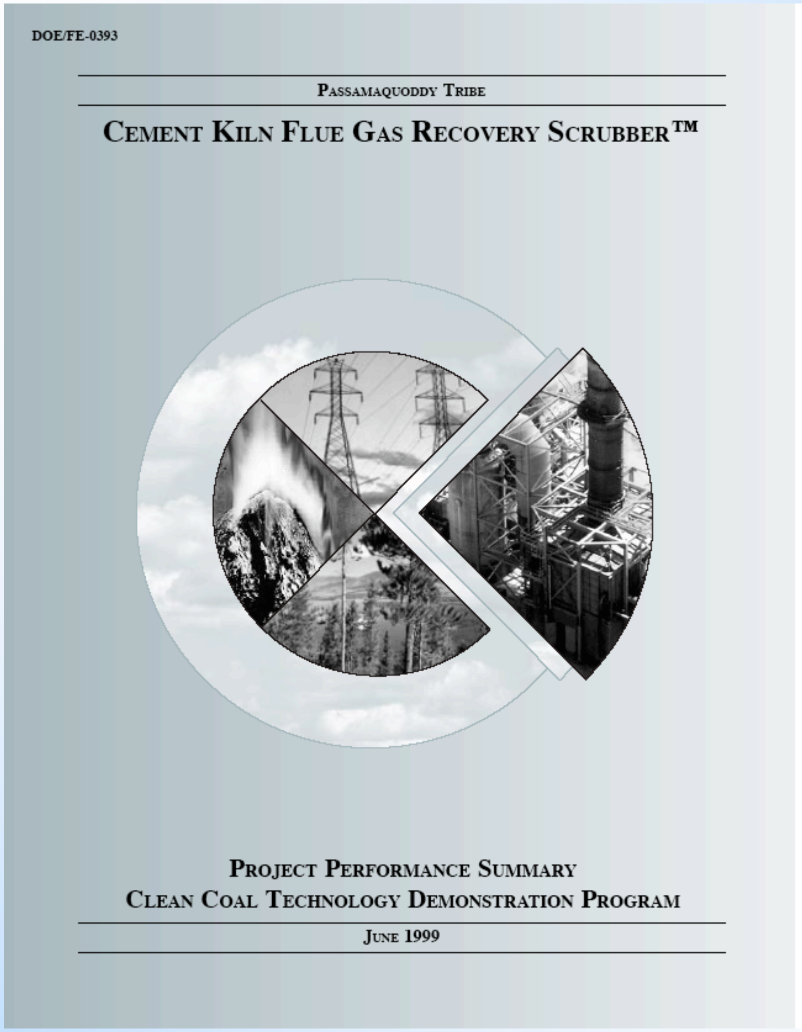
Features:

- 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
- Retrofitable 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



DOE/FE-0393

Passamaquoddy Tribe

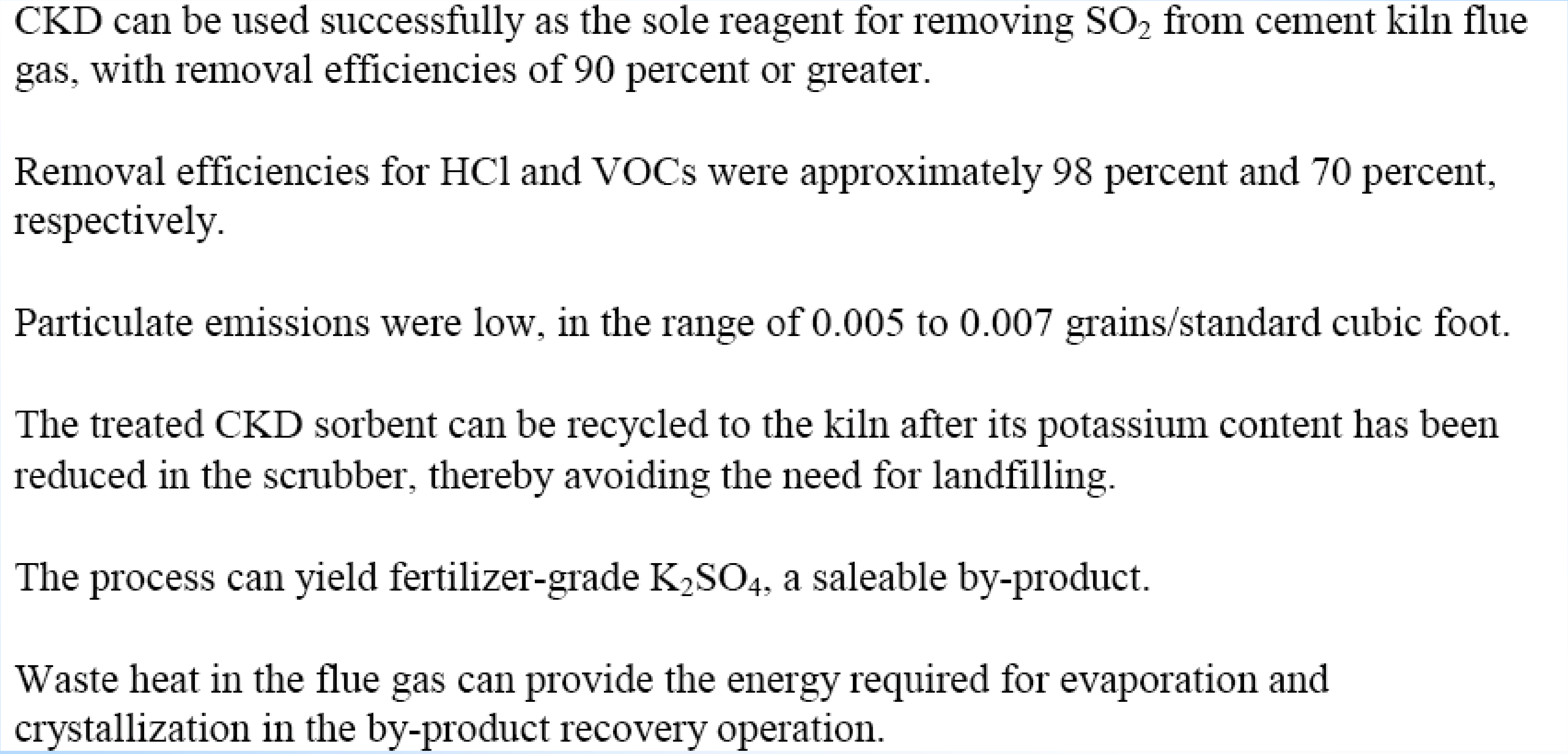
Cement Kiln Flue Gas Recovery Scrubber™

Project Performance Summary
Clean Coal Technology Demonstration Program

June 1999

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 SO_2 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.

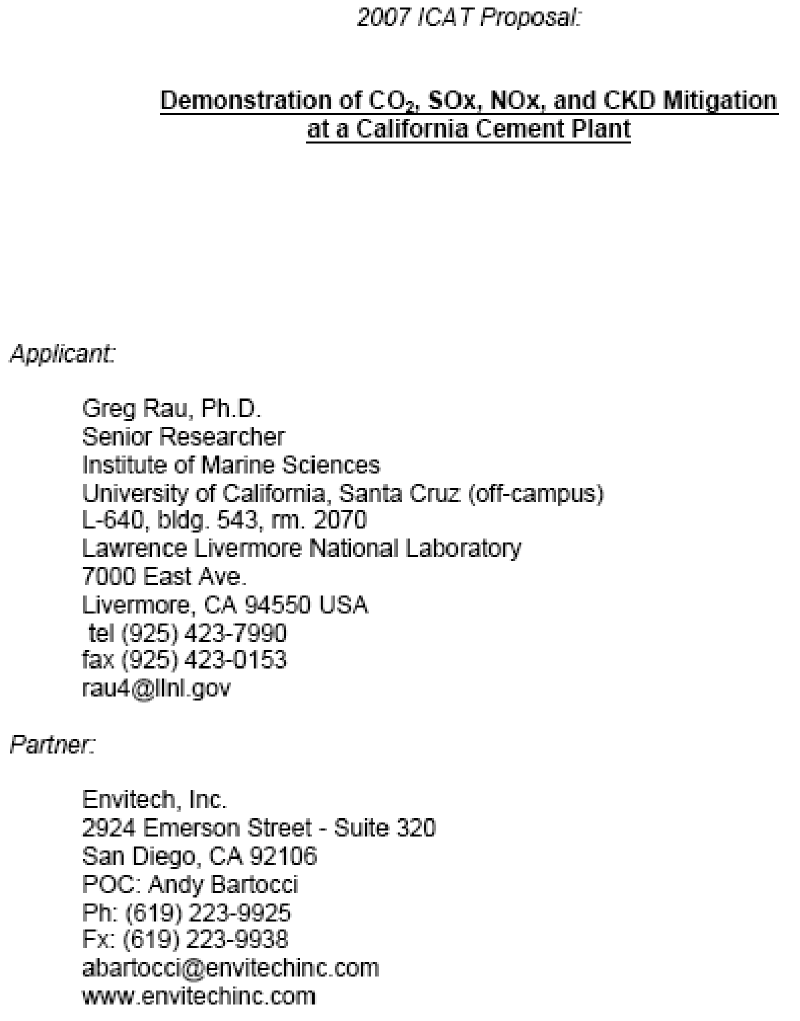
The treated CKD sorbent can be recycled to the kiln after its potassium content has been reduced in the scrubber, thereby avoiding the need for landfilling.

The process can yield fertilizer-grade K_2SO_4, 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 where not funded:



2007 ICAT Proposal:

Demonstration of CO_2, 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) 223-9938
abartocci@envitechinc.com
www.envitechinc.com

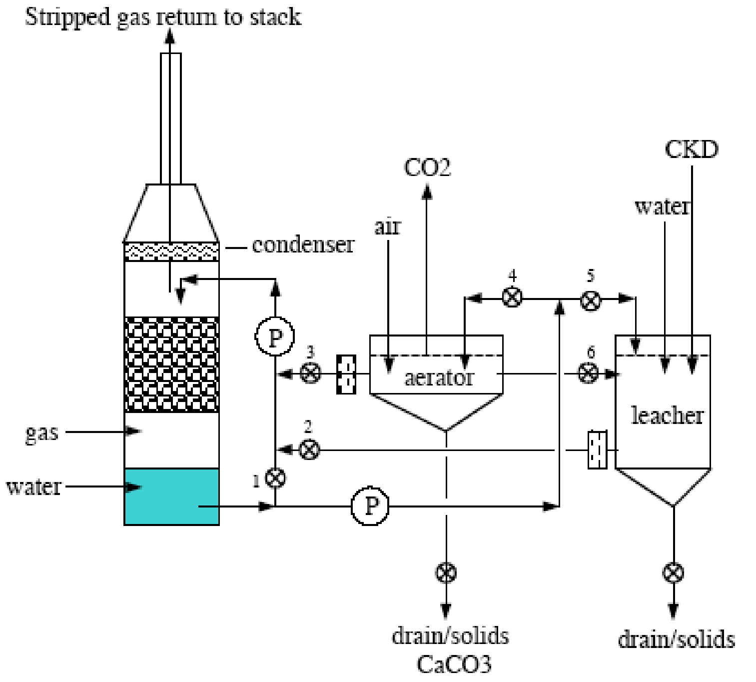
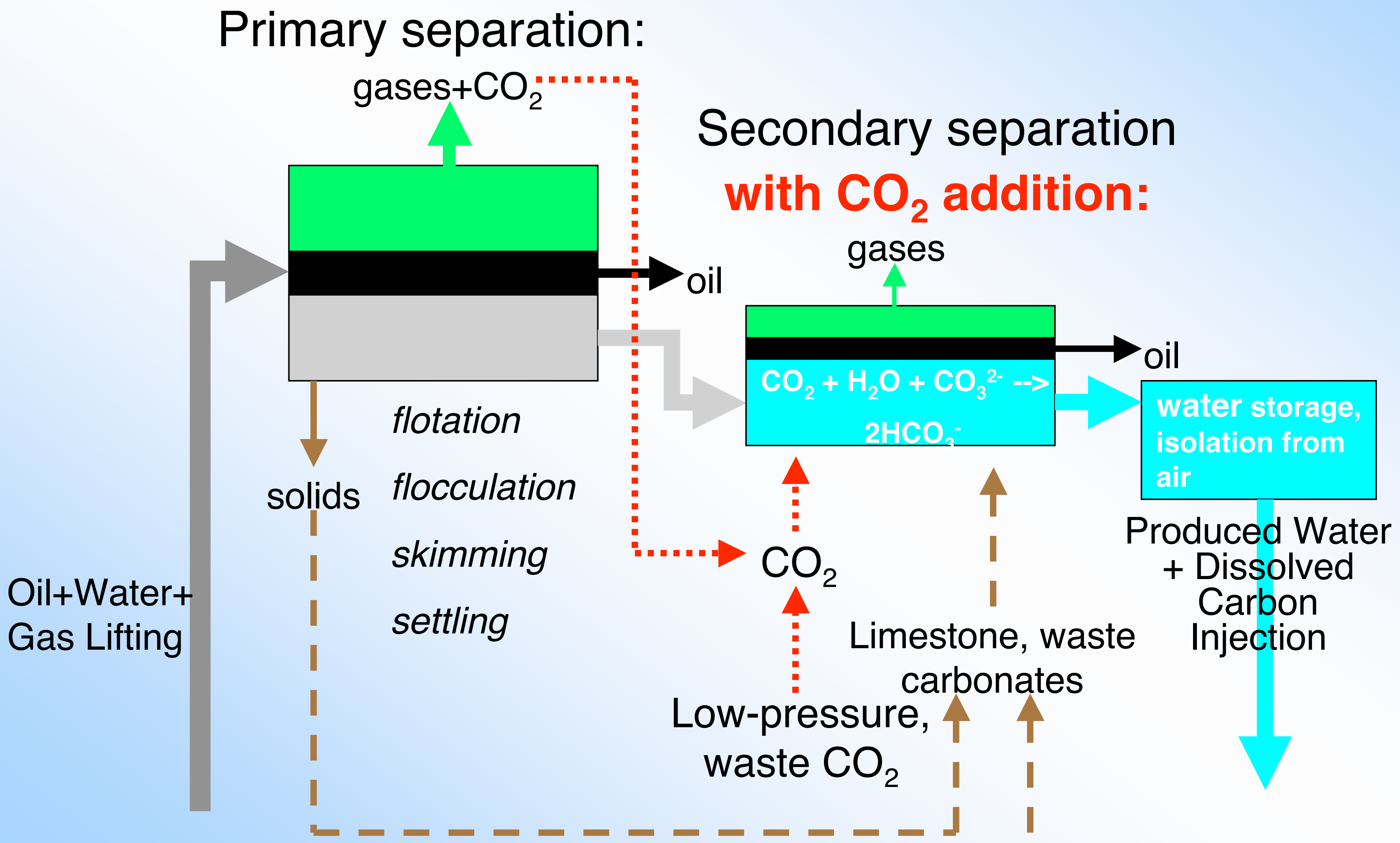


Figure 2. Schematic of demonstration set-up involving CKD solubulization, alkaline solution generation, alkaline stripping of acid flue gas in a scrubber, and precipitation of useable/storable/recyclable products. The system will be designed and built by Envitech, Inc.

Other Aqueous Chemistry-Based CO_2 Mitigation Ideas---->

Produced Water Re-injection with CO_2 Capture + Geologic Storage:



Primary separation:

gases+CO_2

oil

solids

flotation

flocculation

skimming

settling

Oil+Water+
Gas Lifting

Secondary separation
with CO_2 addition:

gases

oil

$CO_2 + H_2O + CO_3^{2-}$ --> $2HCO_3^-$

water storage, isolation from air

CO_2

Low-pressure,
waste CO_2

Limestone, waste
carbonates

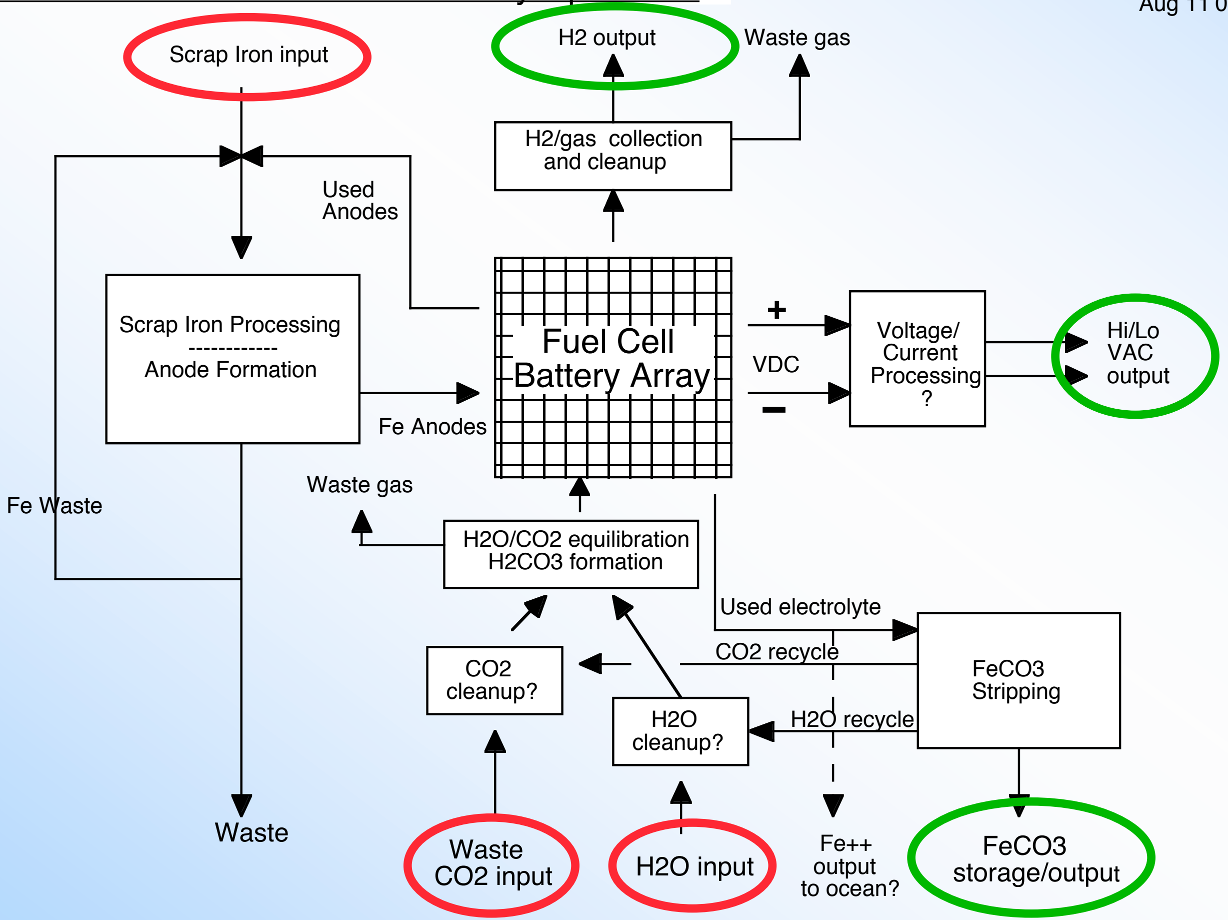
Produced Water
+ Dissolved
Carbon
Injection

Use of CO_2 as an oxidant in an Fe fuel cell:

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

Schematic of Fe/CO2 Fuel Cell Battery Operation:

G.H. Rau
Aug 11'03



Scrap Iron input

H2 output

Waste gas

H2/gas collection and cleanup

Used Anodes

Scrap Iron Processing

Anode Formation

Fe Anodes

Fuel Cell Battery Array

+

VDC

−

Voltage/ Current Processing ?

Hi/Lo VAC output

Fe Waste

Waste gas

H2O/CO2 equilibration H2CO3 formation

Used electrolyte

CO2 recycle

FeCO3 Stripping

CO2 cleanup?

H2O cleanup?

H2O recycle

Waste

Waste CO2 input

H2O input

Fe++ output to ocean?

FeCO3 storage/output

Figure 1

Fe/CO_2 Fuel Cell Requirements, Yields, Costs

Mass in (tonnes):

1 Fe^0 -->

0.79 CO_2 -->

0.32 H_2O -->

Fuel cell

Mass/energy out:

--> 2.07 $FeCO_3$

--> 0.04 H_2

--> 300 kWh_e

Cost per tonne Fe:

\$100 Fe^0 -->

\$30 COM -->

Fuel cell

Output value per tonne Fe:

--> \$15 CO_2 avoid.(@\$20/tonne)

--> \$60 H_2 (@\$1.50/kg H_2)

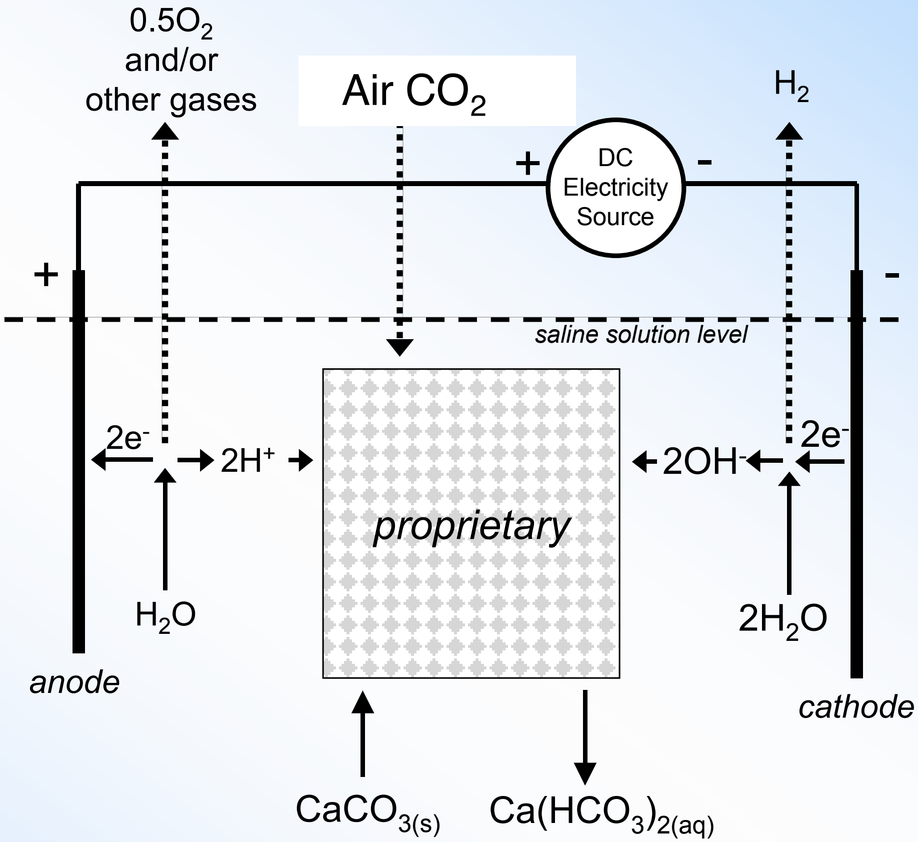
--> \$15 elect. (@\$0.05/kWh)

Net cost = (\$130-\$90)/0.79 = \$50/tonne CO_2 mitigated?

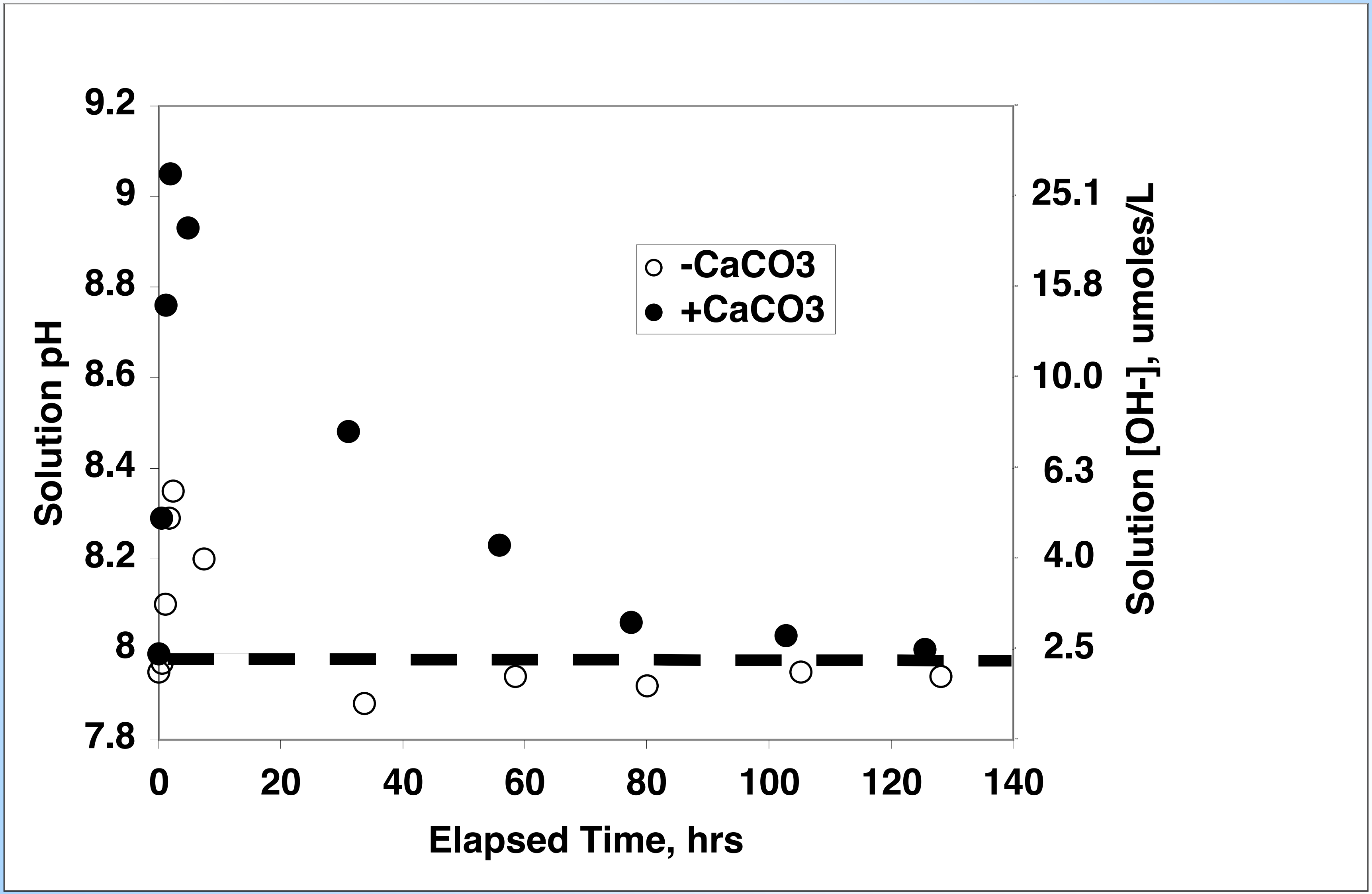
Electrochemical production of alkalinity for CO_2 mitigation and carbon-negative H_2 production

Use renewable DC electricity to allow:

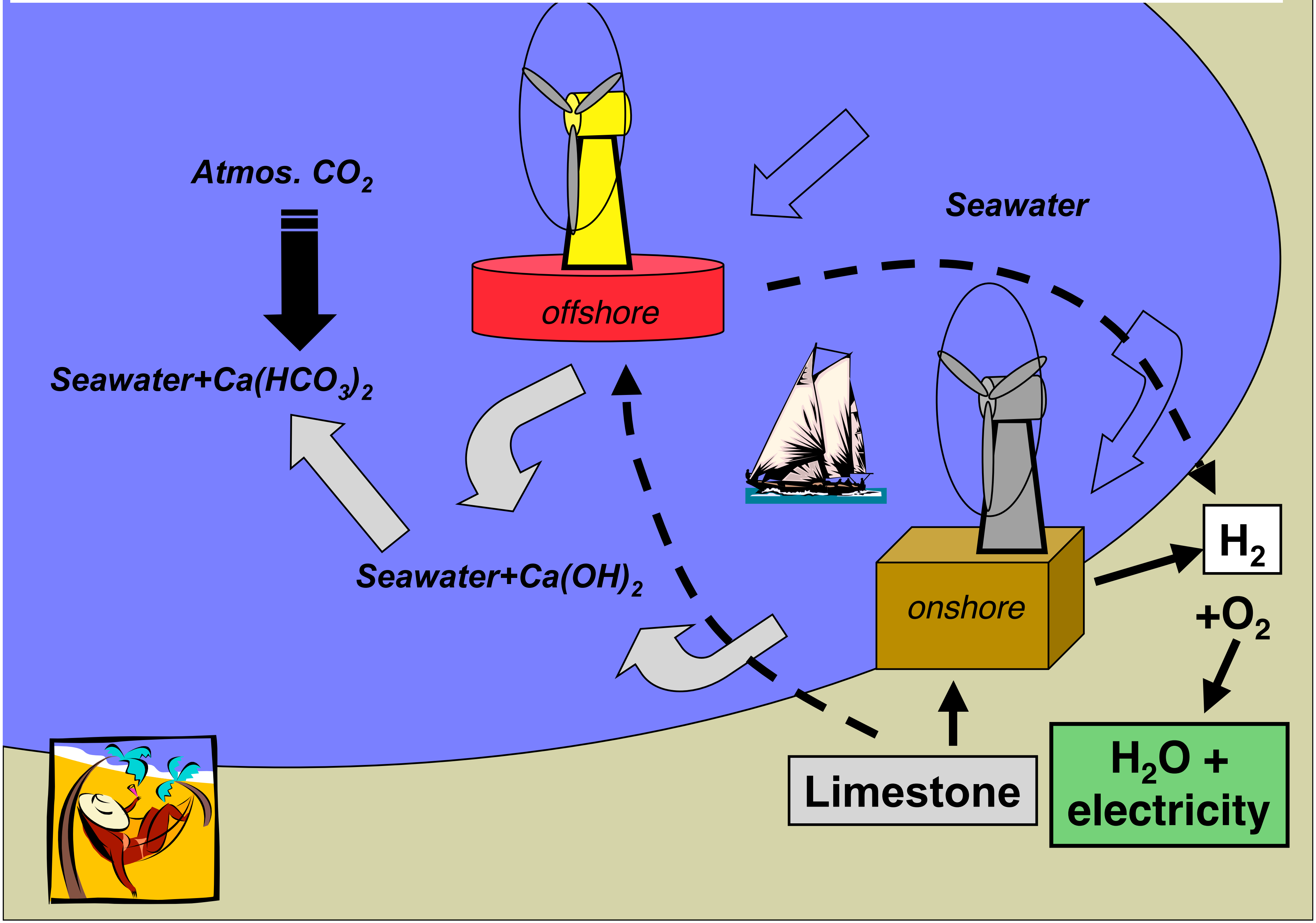
- ❑ Production of air CO_2 absorbing solutions while generating “green” hydrogen.
  - ➢ 22 tonnes CO_2 absorbed per tonne H_2 produced
  - ➢ thus, novel production of <u>carbon-negative hydrogen</u>.
- ❑ Addition of alkalinity to seawater neutralizes or offsets ocean acidity.



Experimental results - Alkalinity generated, air CO_2 absorbed



For Example: Ocean-based, carbon-negative wind hydrogen



Atmos. CO_2

Seawater

offshore

Seawater+$Ca(HCO_3)_2$

Seawater+$Ca(OH)_2$

onshore

H_2

$+O_2$

Limestone

H_2O + electricity

Conclusions:

- Continued reliance on fossil fuel energy in a carbon-constrained world requires that multiple, cost-effective and safe CO_2 sequestration technologies be quickly found and deployed.
- For point source mitigation, relying solely on the capture and storage of CO_2 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.