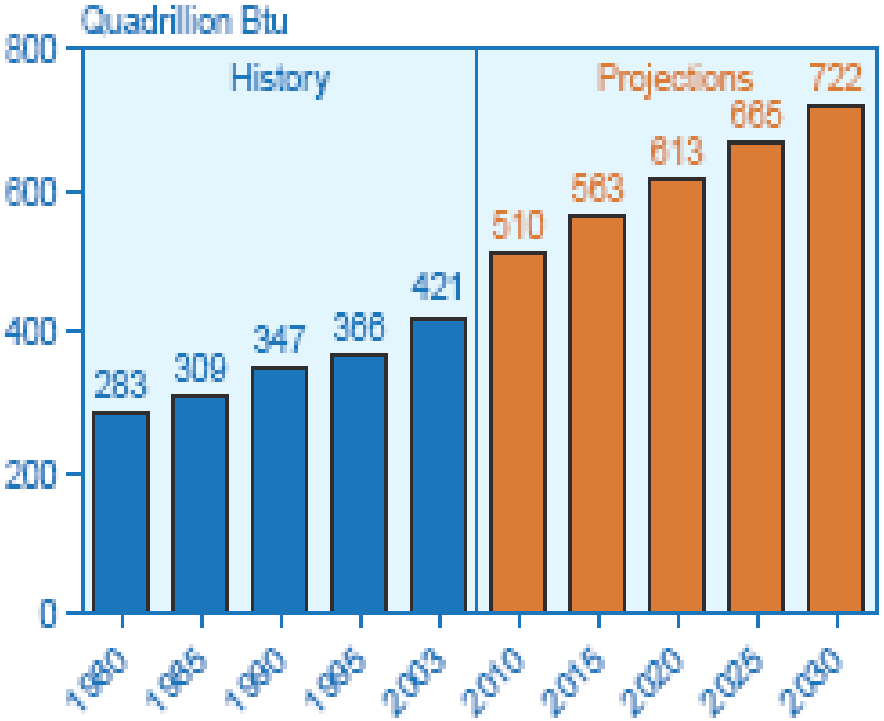
Enabling Sustainable Development of Fossil Fuel Energy Conversion Systems:

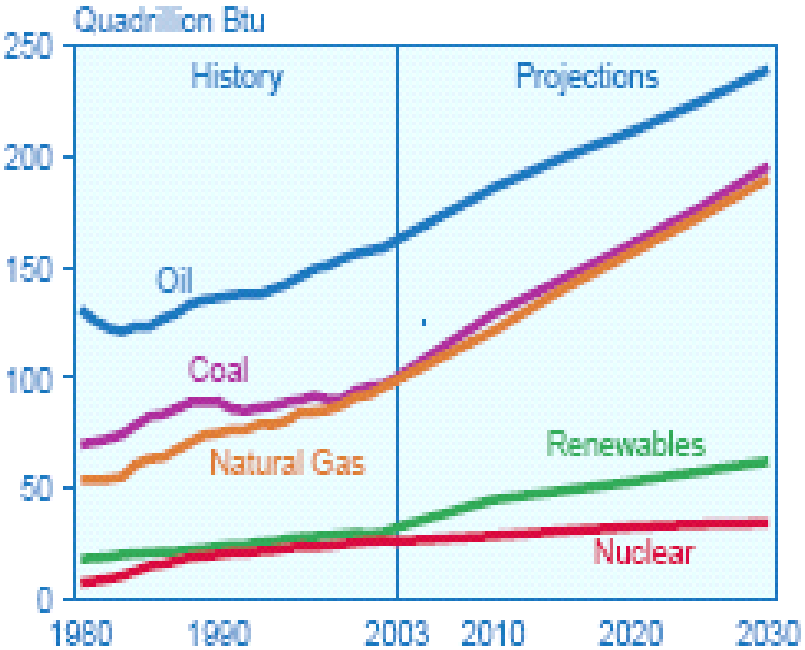
Carbon Mineral Sequestration

Ah-Hyung Alissa Park
Earth and Environmental Engineering
Lenfest Center for Sustainable Energy
Columbia University

2nd U.S.-China Symposium on CO_2 Emissions Control Science & Technology
May 30th, 2008

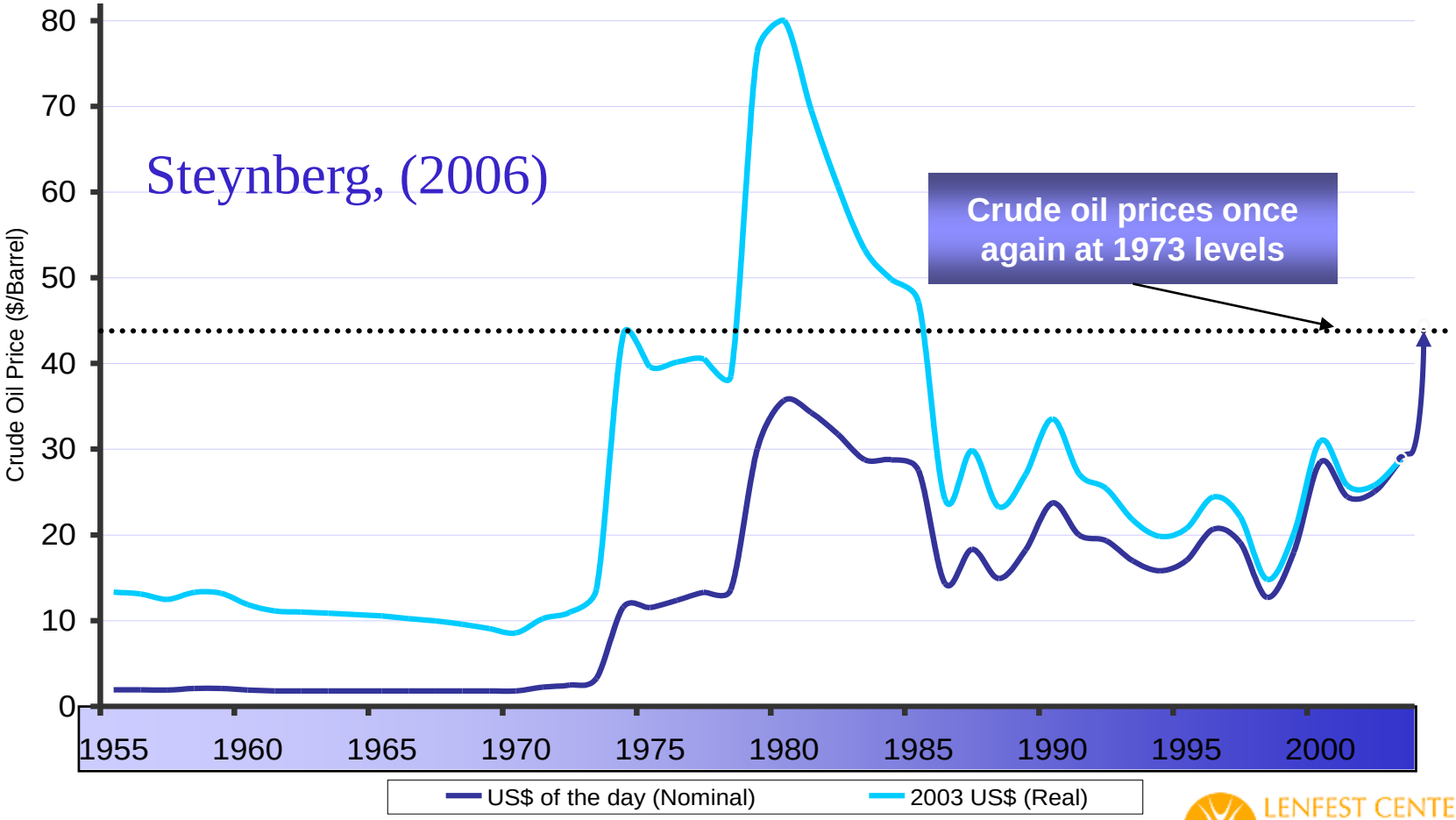
Projected Global Energy Demand & Supply





Source: International Energy Outlook-2006 Report #:DOE/EIA-0484 (June 2006)

Petroleum-based vs. Synthetic Liquid Fuels



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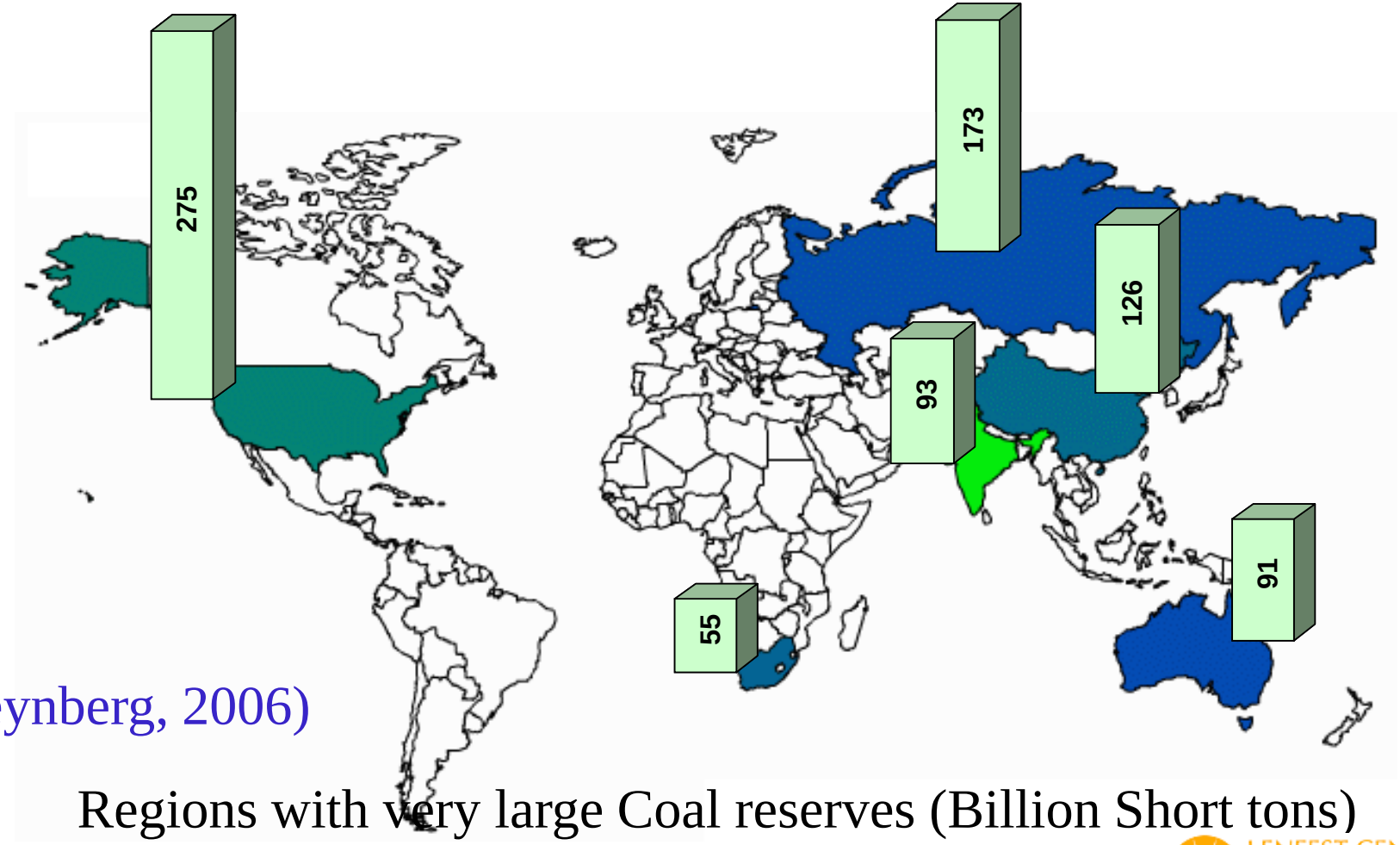
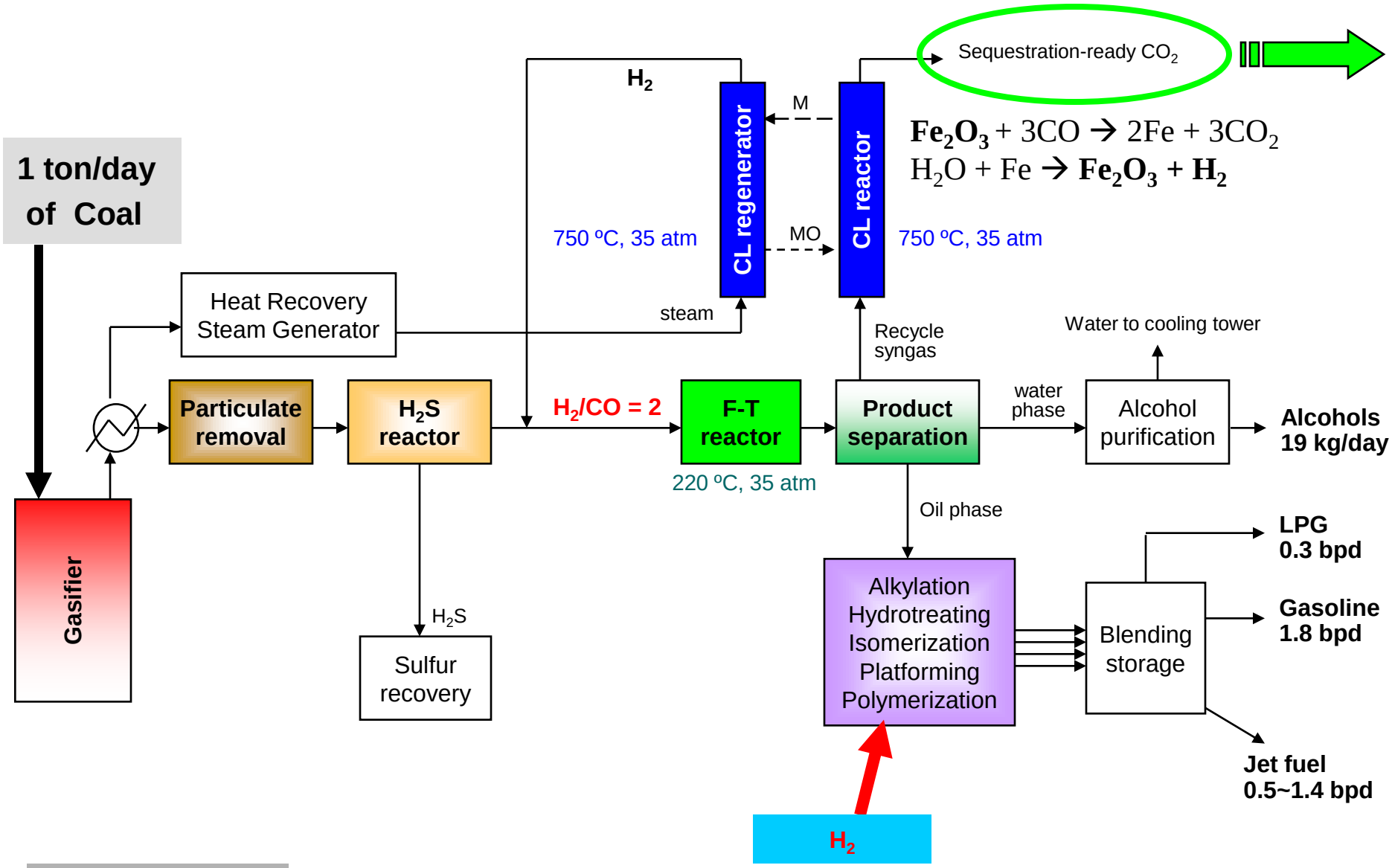
Where could CTL Work?



(Steynberg, 2006)

Regions with very large Coal reserves (Billion Short tons)

Coal-to-Liquid process using Chemical Looping process



OSU Process

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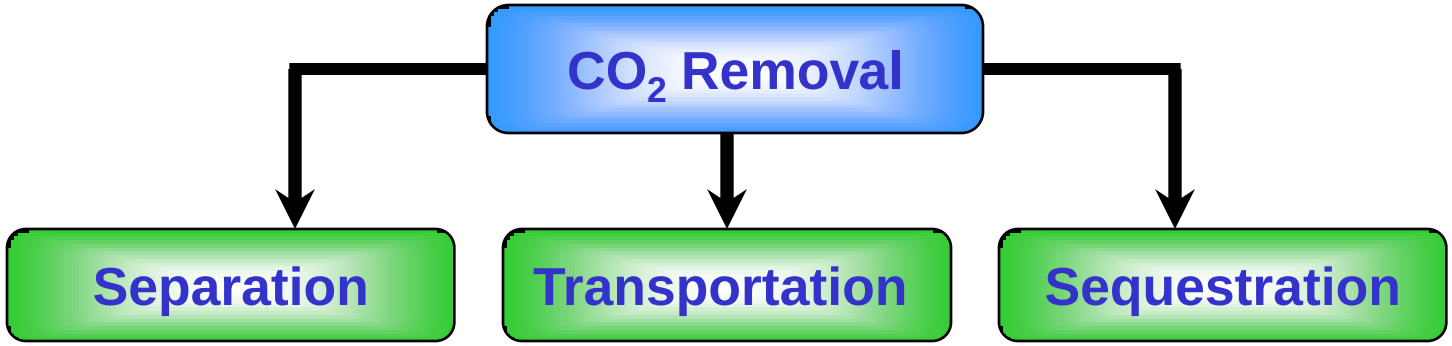
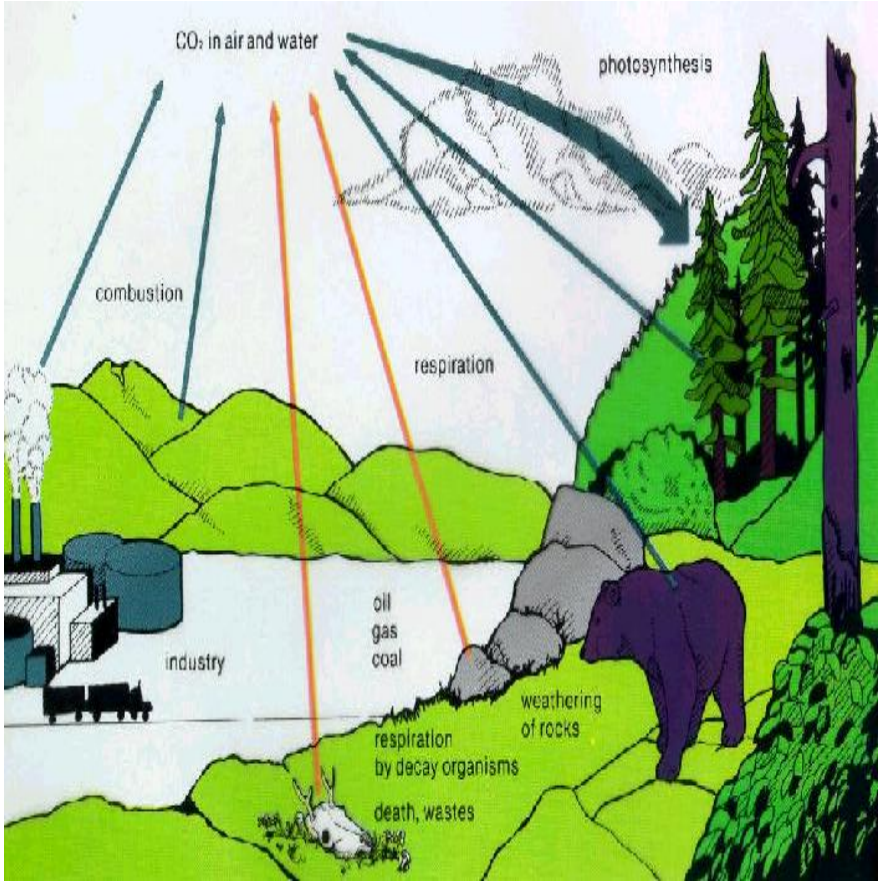
Carbon Dioxide Sequestration Options



- Necessary Characteristics
  - Capacity and price
  - Environmentally benign fate
  - Stability

Carbon Dioxide Disposal Options

- Geological sequestration
- Ocean sequestration
- Biological sequestration
- Mineral sequestration
  - Safe and permanent



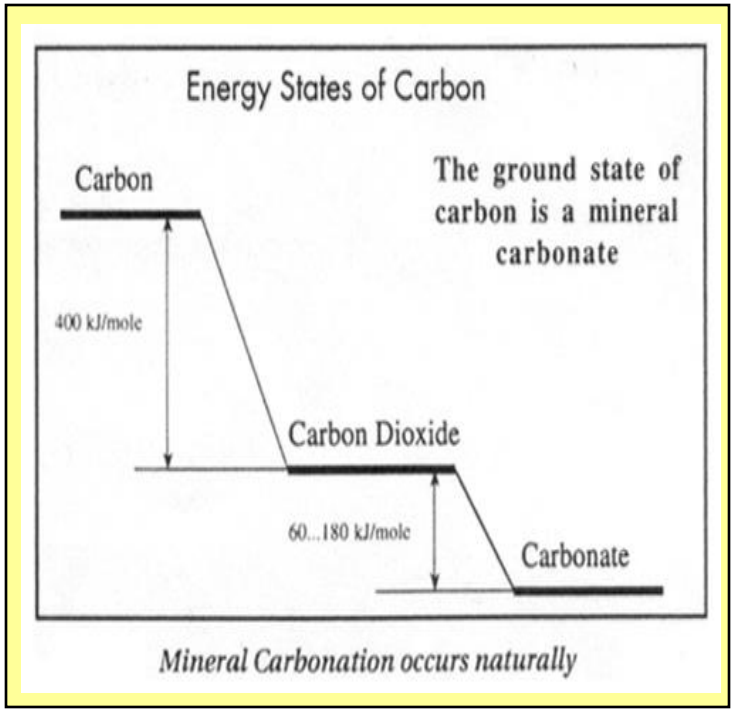
Killer Lake

In 1986, a tremendous explosion of CO_2 from the lake Nyos, West of Cameroon, killed more than 1700 people and livestock up to 25 km away. Both lakes still contain huge amounts of CO_2 (10 and 300 millions m^3 in Monoun and Nyos, respectively)

21m high self-sustained soda fountain
Photo: Bernard Canet, March 1995

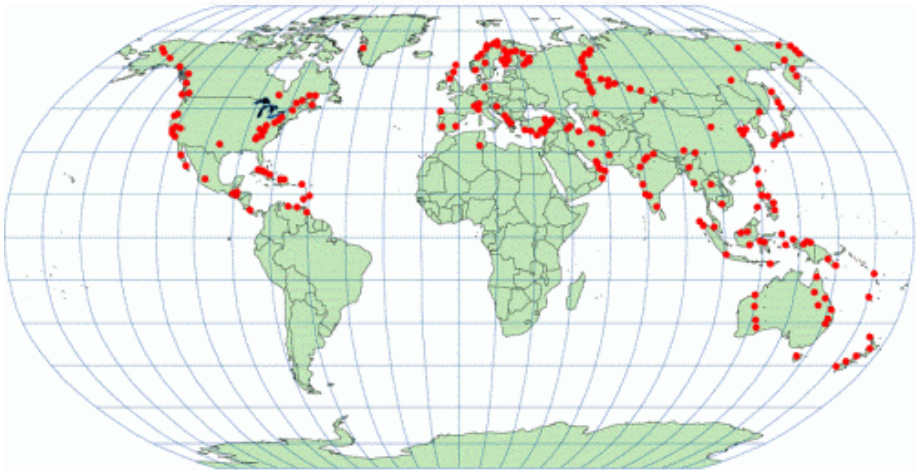
Mineral Sequestration of CO_2

- Mimics natural chemical transformation of CO_2
  $MgO + CO_2 \rightarrow MgCO_3$
- Thermodynamically stable product
- Exothermic transformation
- Appropriate for long-term environmentally benign and unmonitored storage



(U.S. DOE, 1999)

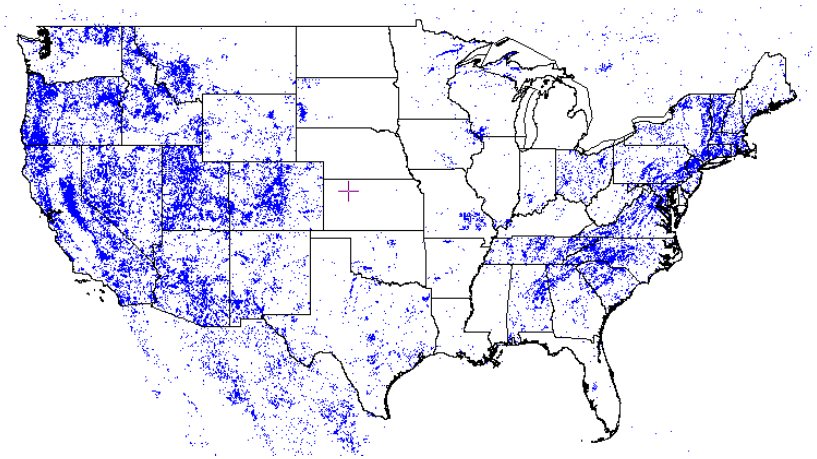
Availability of Minerals



Serpentinite Ore Bodies

Mg resources that far exceed world wide coal reserves (10,000 Gt)

World-wide distribution of Mg-rich ultramafic rocks (Los Alamos National Laboratory)



Rockville Quarry, Maryland (May 1999)

Direct Carbonation Studies: G-S reaction

Olivine reaction:

$$Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2$$

Mineral size < 125 μm

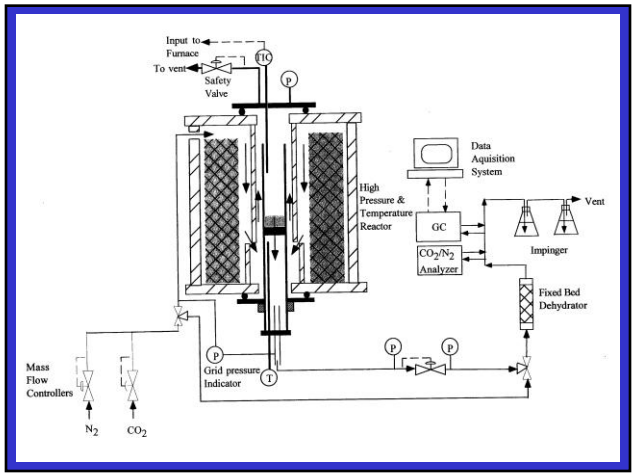
(1) P_{CO2} = 1 atm; T = 350 °C; Time = 24 hr

(2) P_{CO2} = 25 atm; T = 350 °C; Time = 8 hr

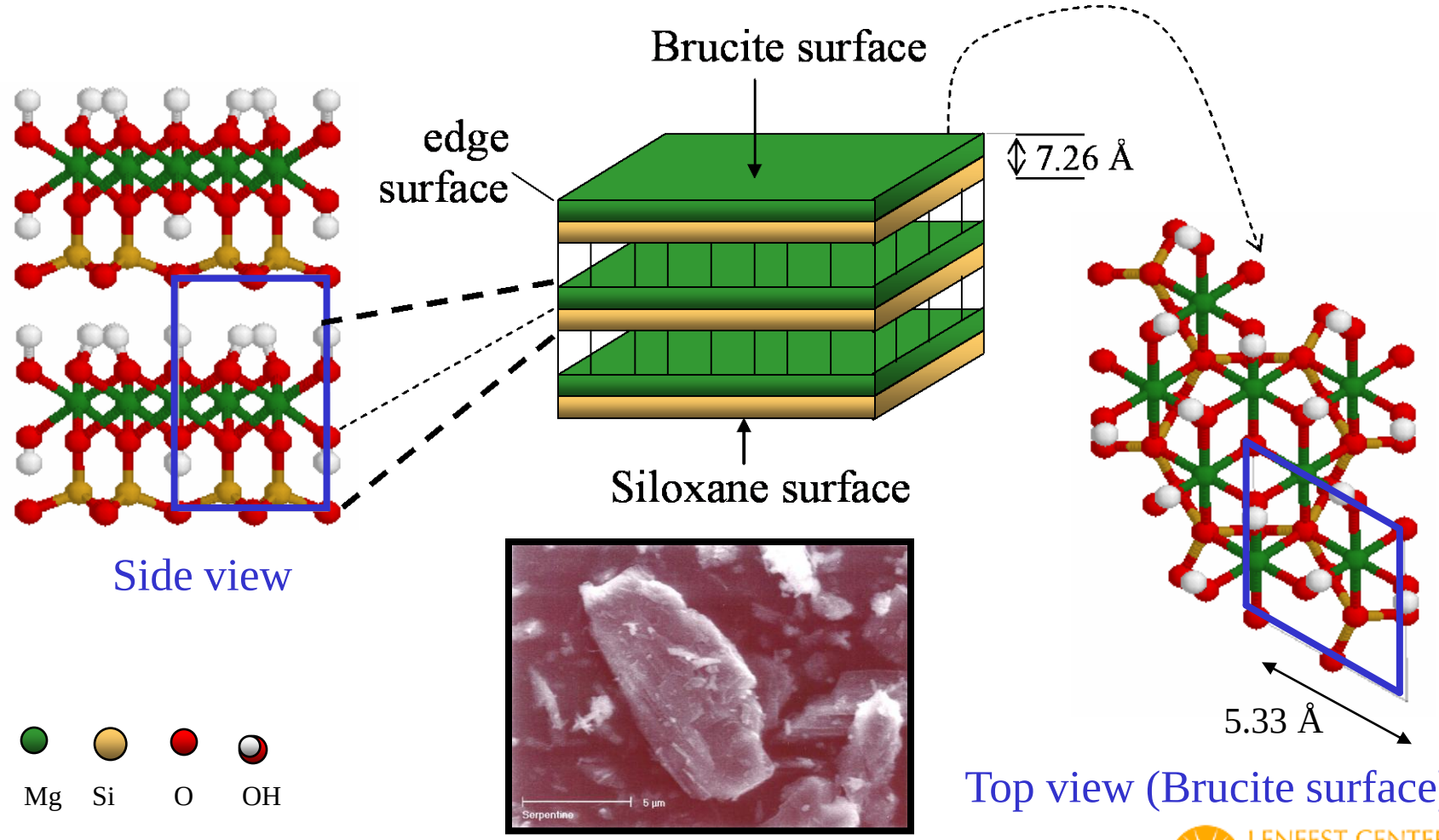
Results:

– no conversion of silicate minerals

– slow kinetics



Structure of Serpentine



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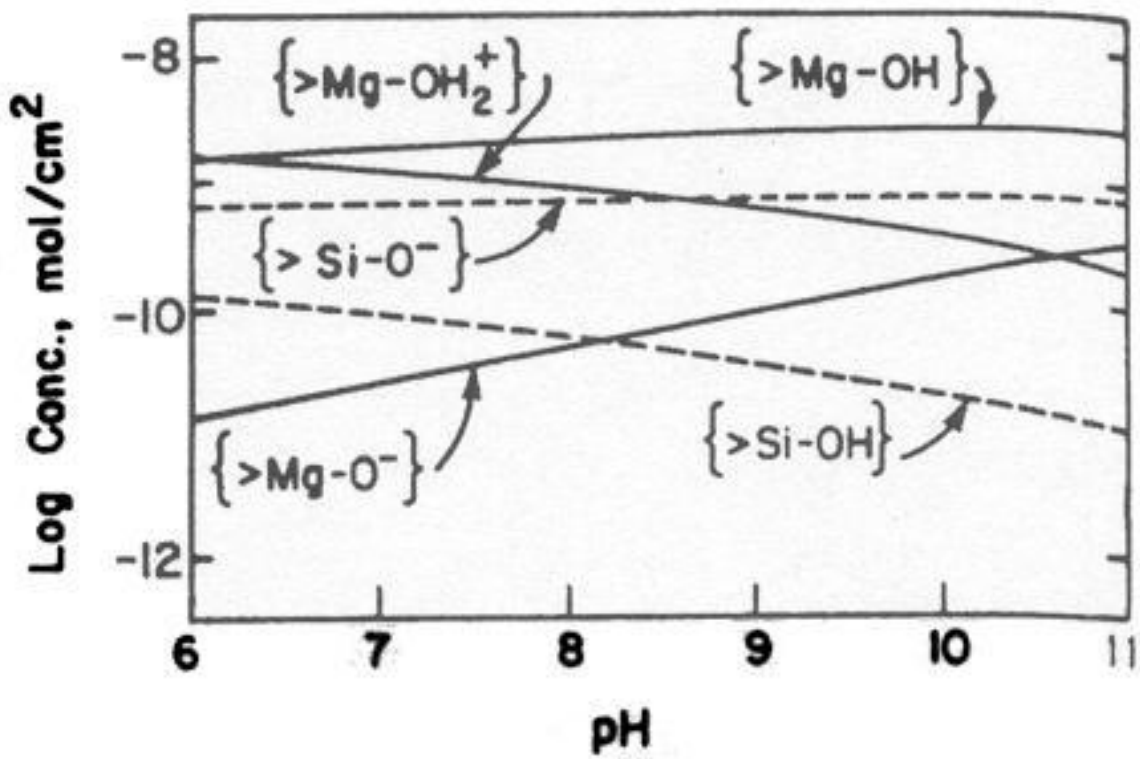
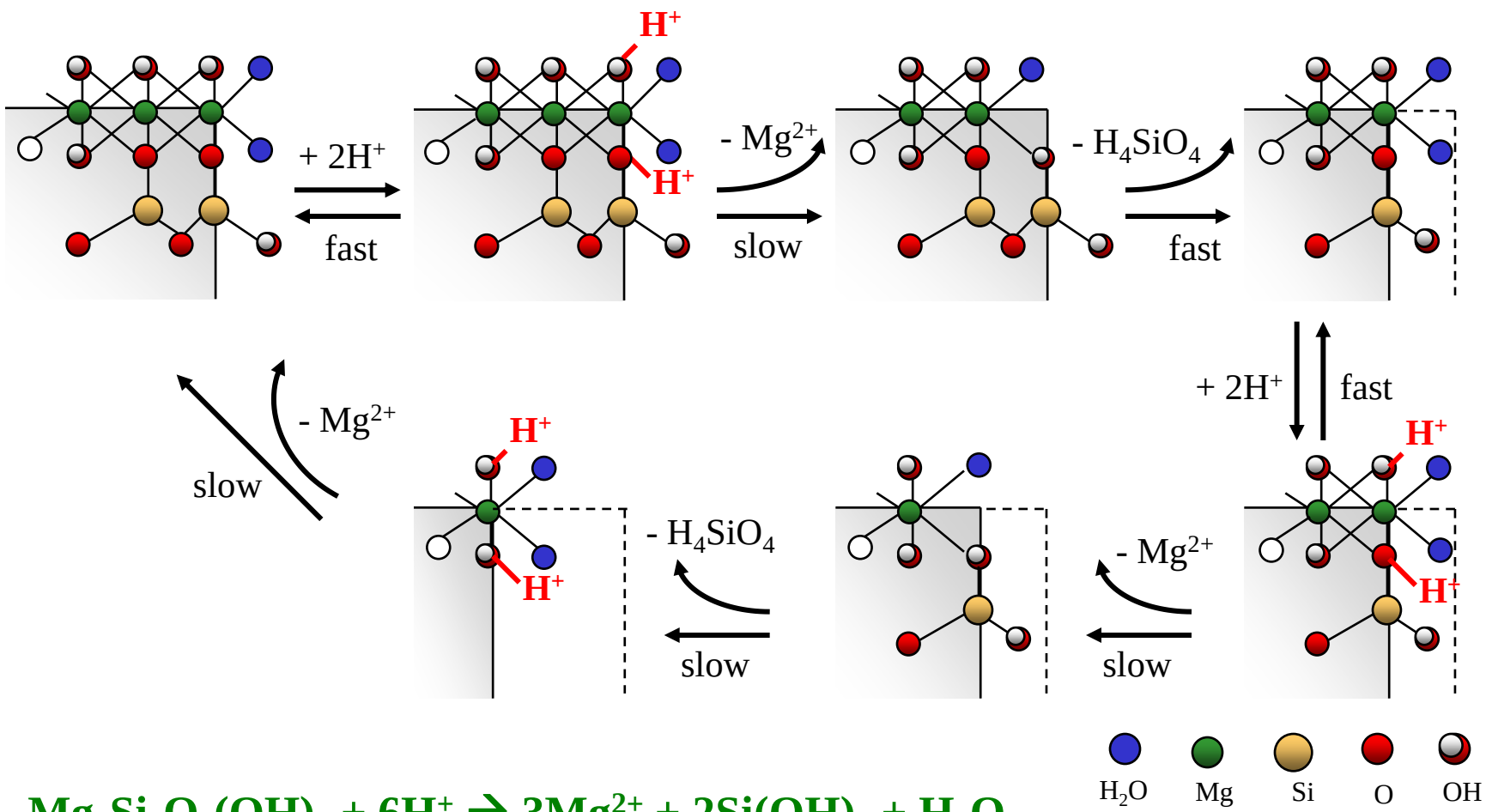
Our Proposed Mechanism of Congruent Dissolution of Serpentine (edge)



Distribution of surface species on chrysotile (Bales and Morgan, 1985)

Our Proposed Mechanism of Congruent Dissolution of Serpentine (edge)



$$Mg_3Si_2O_5(OH)_4 + 6H^+ \rightarrow 3Mg^{2+} + 2Si(OH)_4 + H_2O$$

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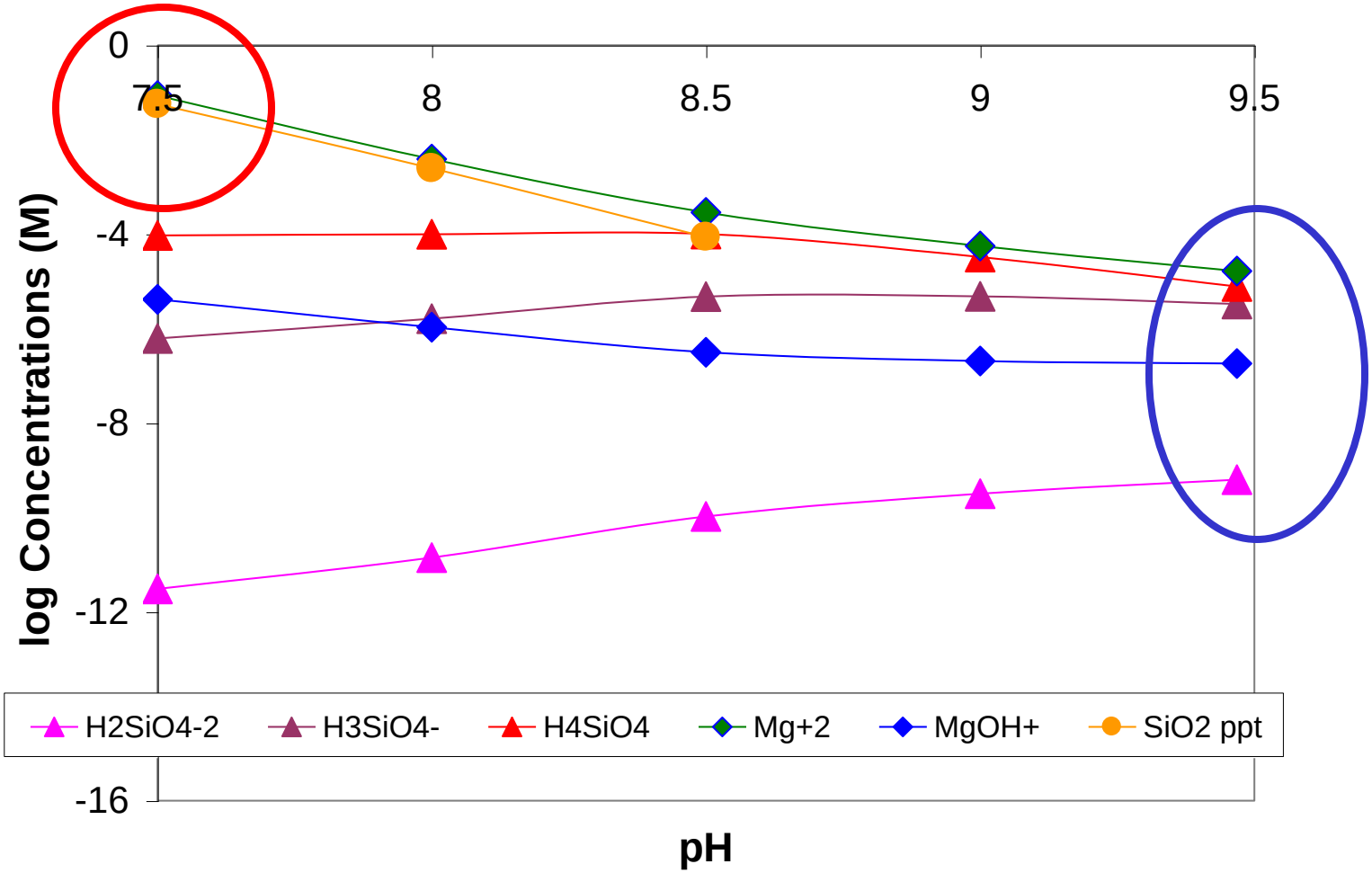
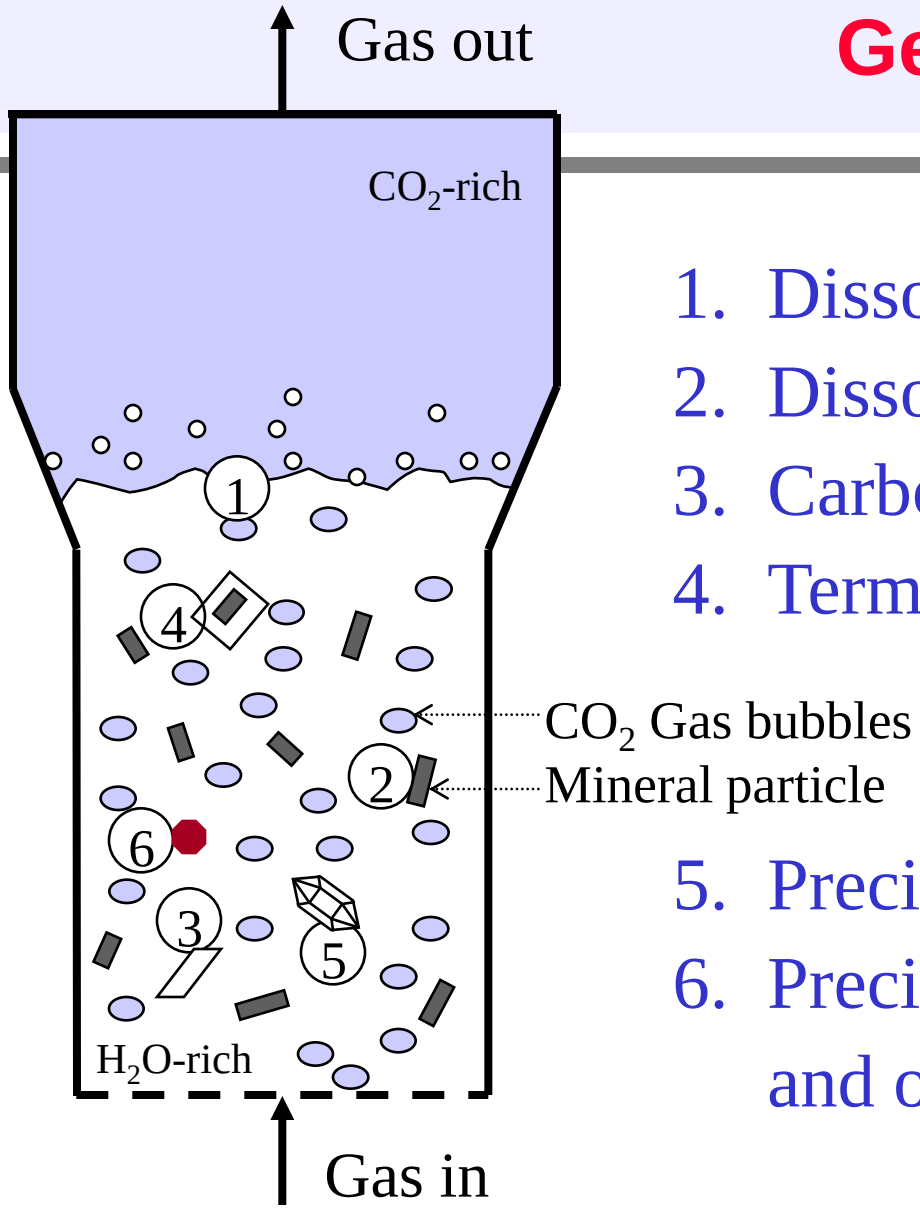
Visual MINTEQ Simulation

Effect of pH on Dissolution of Serpentine



Effect of pH on chrysotile (serpentine) dissolution (P_{CO2} = 0, T = 25 ℃)

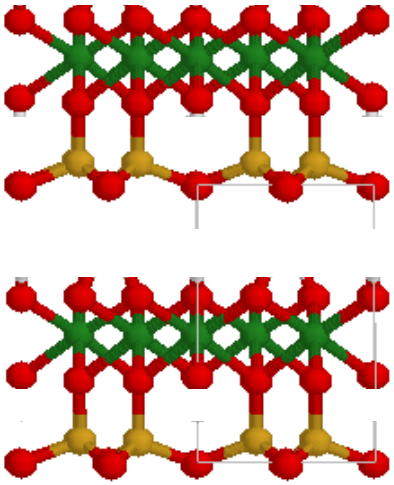
Geochemical Model

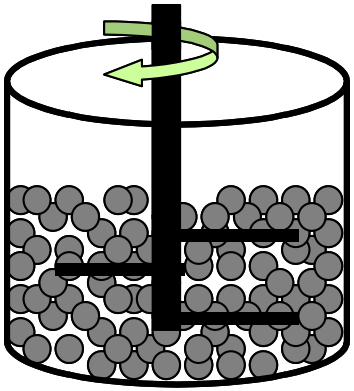


1. Dissolution of CO_2
2. Dissolution of mineral*
3. Carbonation/Precipitation
4. Termination of reaction
5. Precipitation of silica phases
6. Precipitation of phases of iron and other minor/trace elements

Enhancement of Mineral Dissolution

- Pretreatment options
  - Heat treatment of serpentine (630 ℃)
  - Dry or wet attrition grinding (< 2 μm)

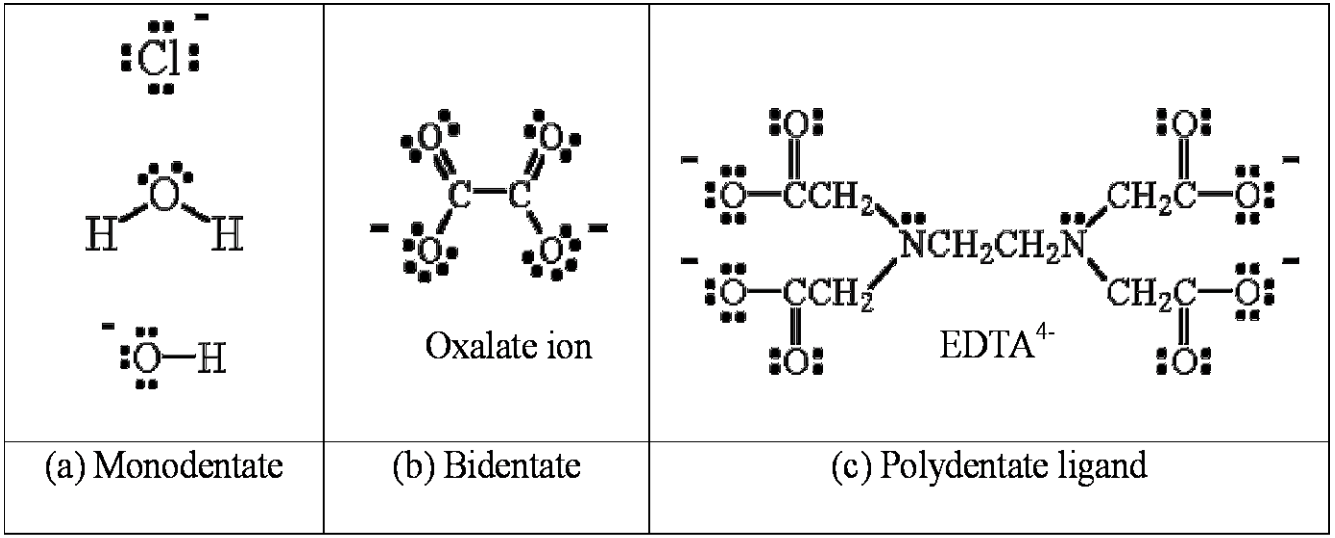


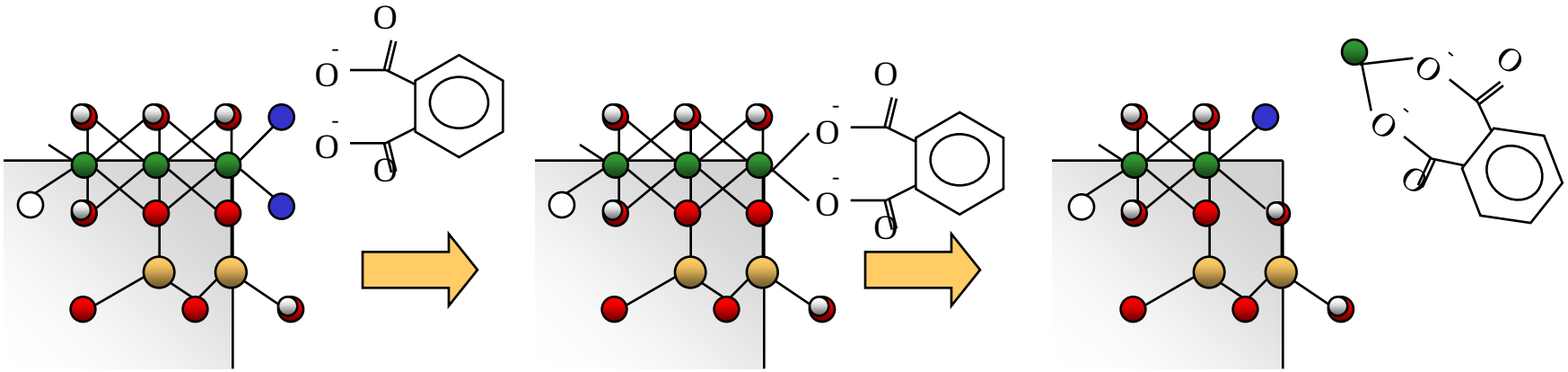


- Chemical additives: Strong acids, $NaHCO_3$/NaCl
- Weak acids

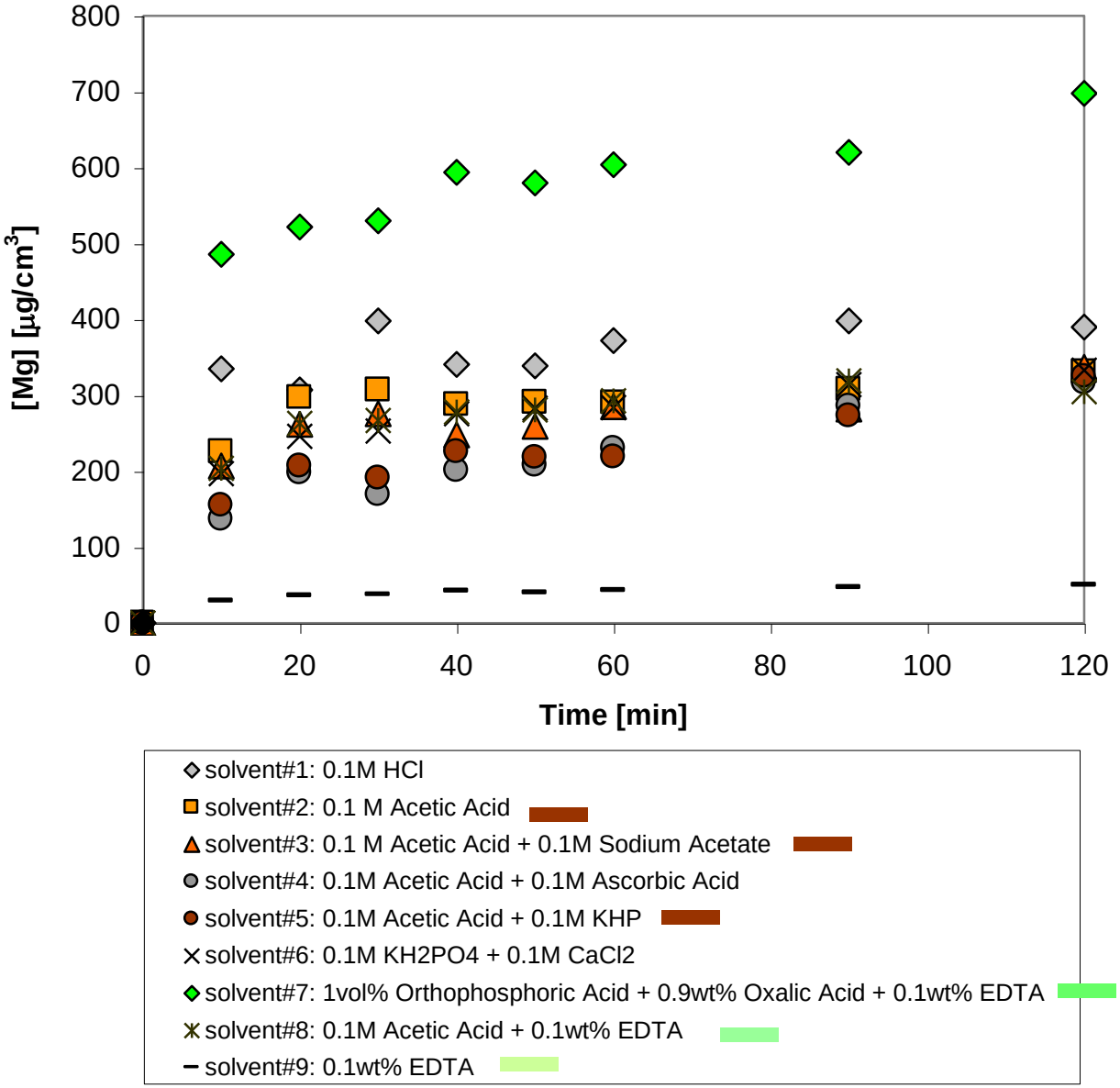
Chemically Enhanced Dissolution of Serpentine

Various Chelating Agents





Potassium acid phthalate KH_2PO_4



Dissolution of mineral

Precipitation of phases of iron and other minor/trace elements

(i.e. Fe – FeO(OH) or Fe_2O_3)

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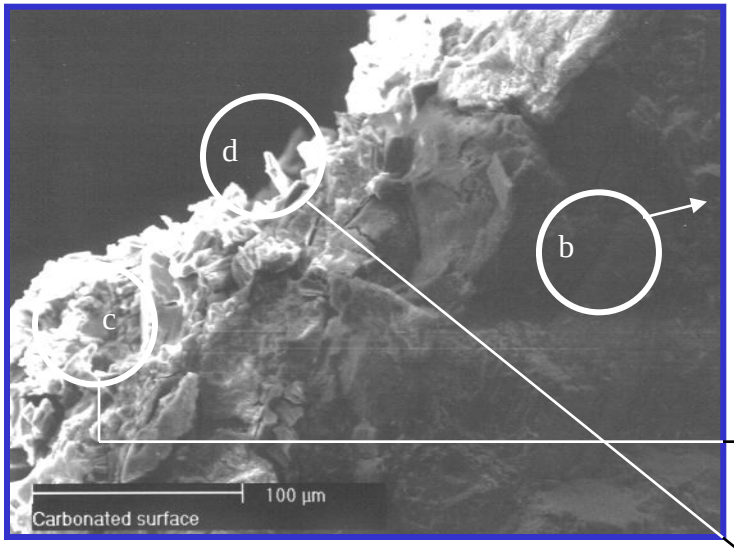
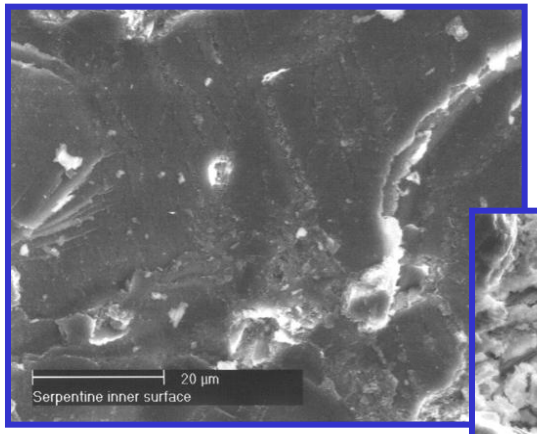
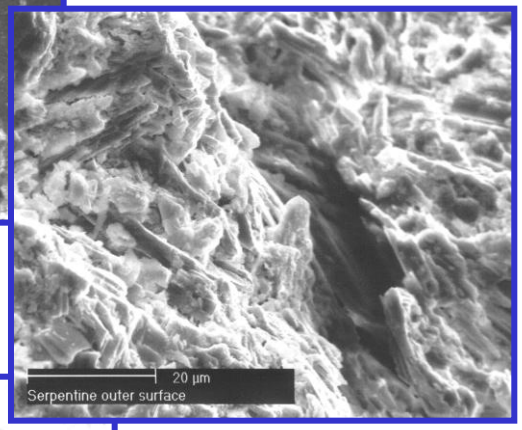
SEM of cross-sectional view of *serpentine* aggregate



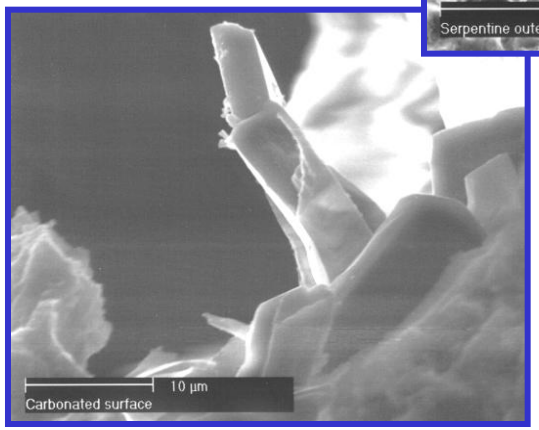
(a) Overall view of cross-sectional area (dissolved and carbonated in solvent#7)



(b) Inner surface

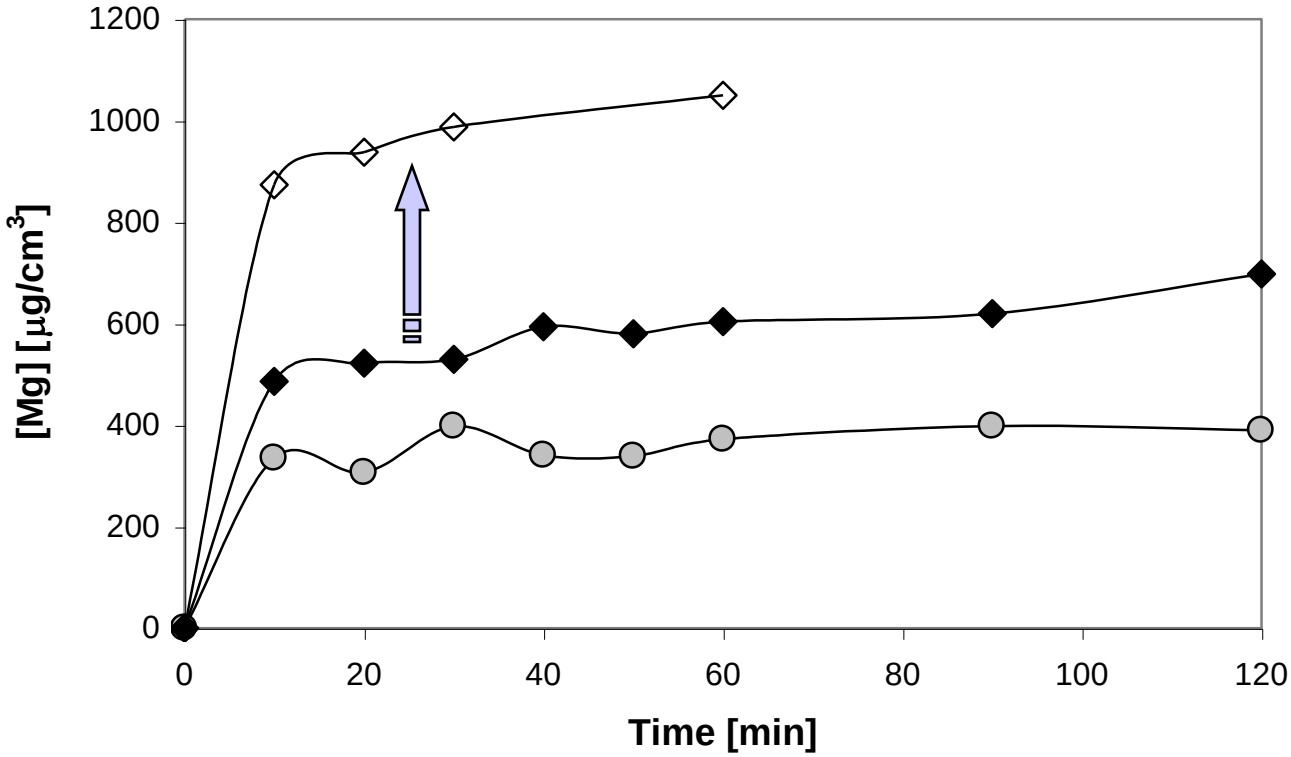


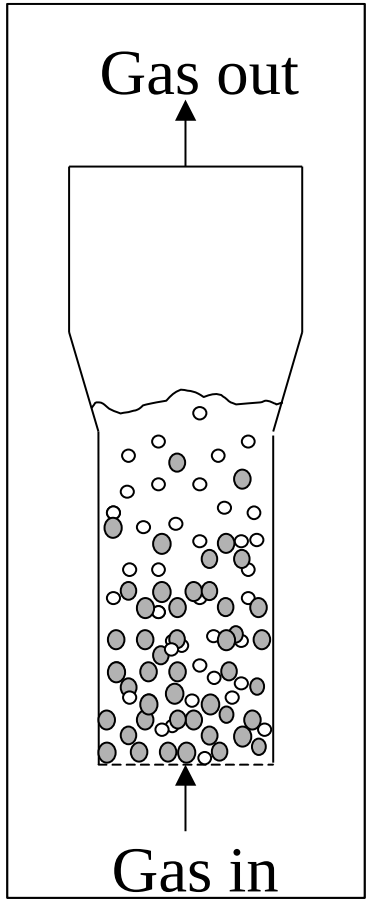
(c) Dissolved outer surface



(d) $MgCO_3$ crystal

Effect of Internal Grinding





- 0.1M HCl w/o internal grinding
- 1vol%Orthophosphoric Acid+0.9wt%Oxalic Acid+0.1wt%EDTA w/o internal grinding
- 1vol%Orthophosphoric Acid+0.9wt%Oxalic Acid+0.1wt%EDTA with internal grinding

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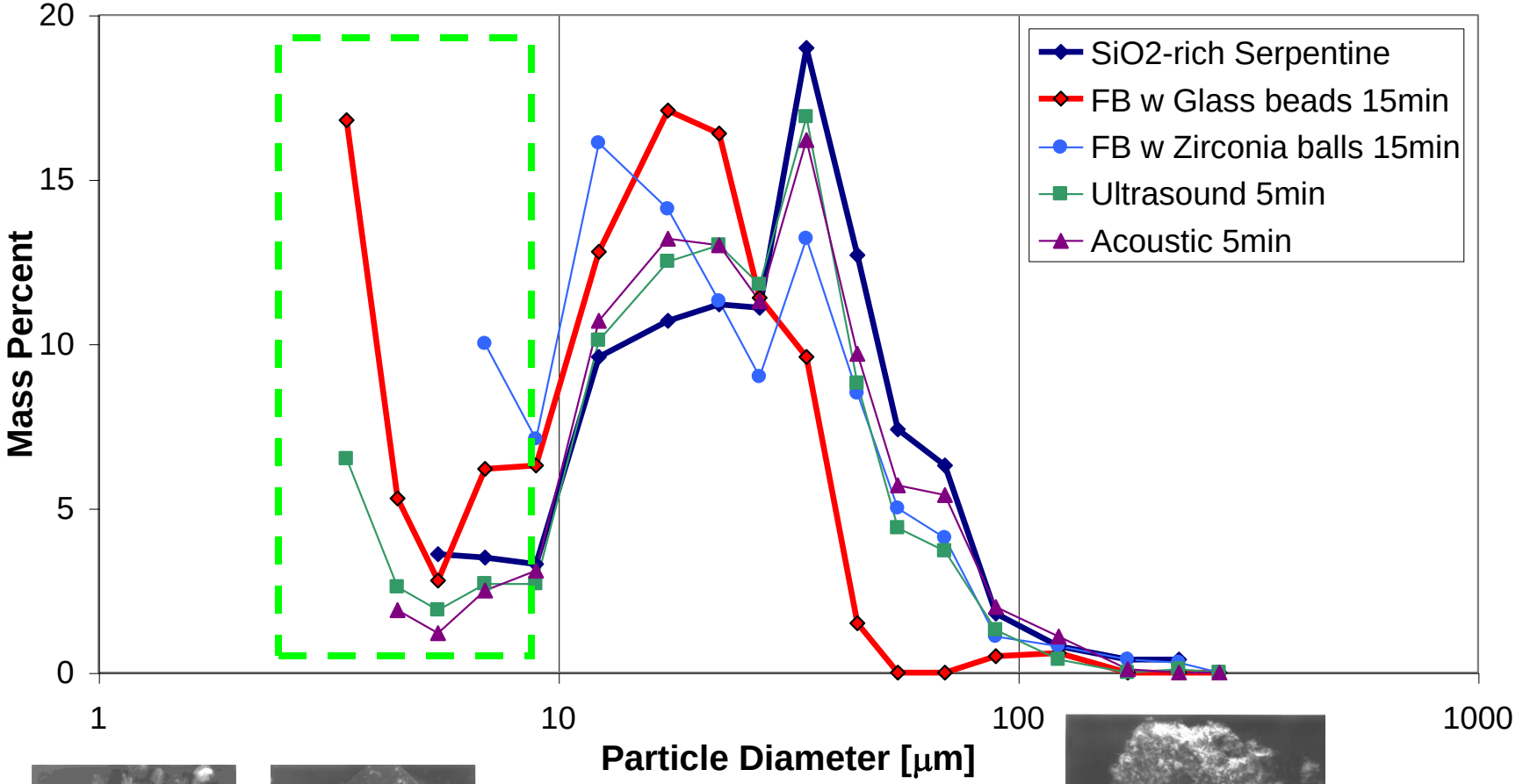
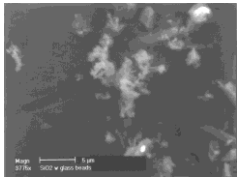
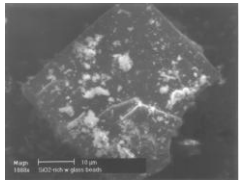
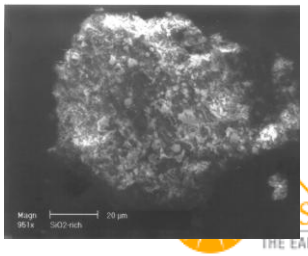
Removal of SiO_2 layer









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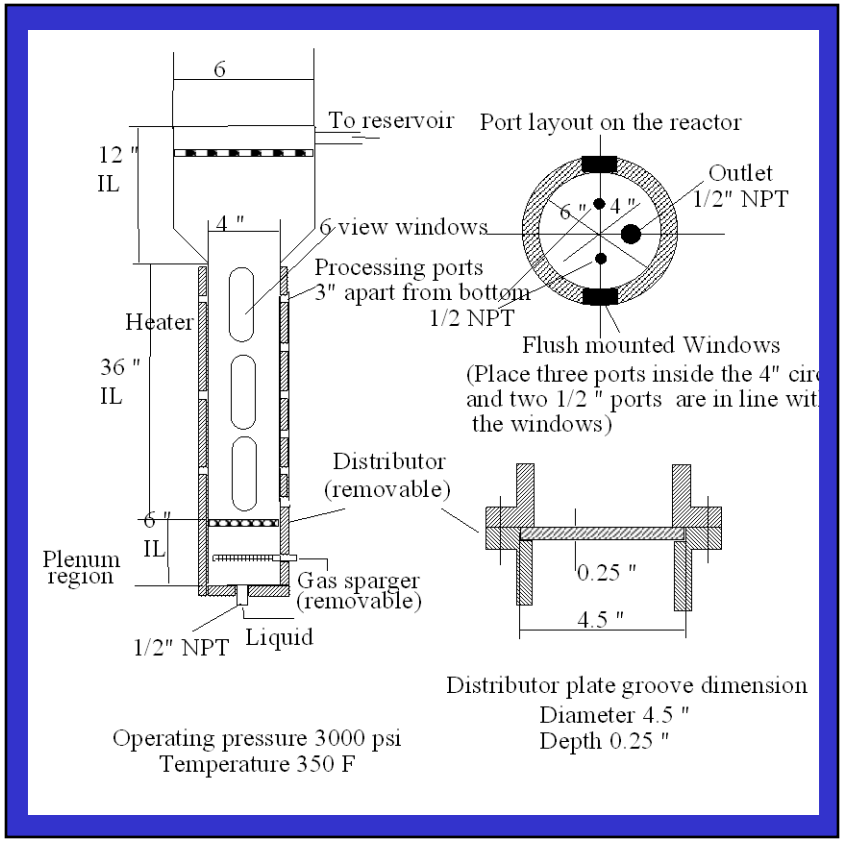
Aqueous Carbonation Studies: G-S-L



High Pressure, High Temperature Three-Phase Fluidized Bed Reactor

- 5 ~ 35 wt% solid
- TGA analysis
- T_{max} = 250 °C
- P_{max} = 210 atm

Aqueous Carbonation Studies

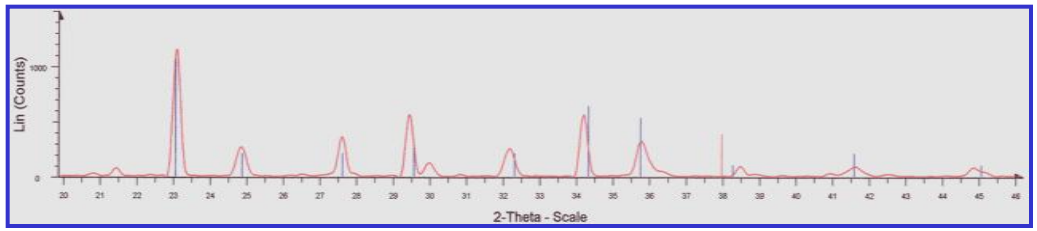
- Reaction Chemistry

  $Mg_3Si_2O_5(OH)_4 + 3CO_2 + 2H_2O \rightarrow 3MgCO_3 + 2H_4SiO_4$

- P = 1000 psig, T = 80° C, $d_p \leq 75$ μm, 5 wt% solid and solvent#7

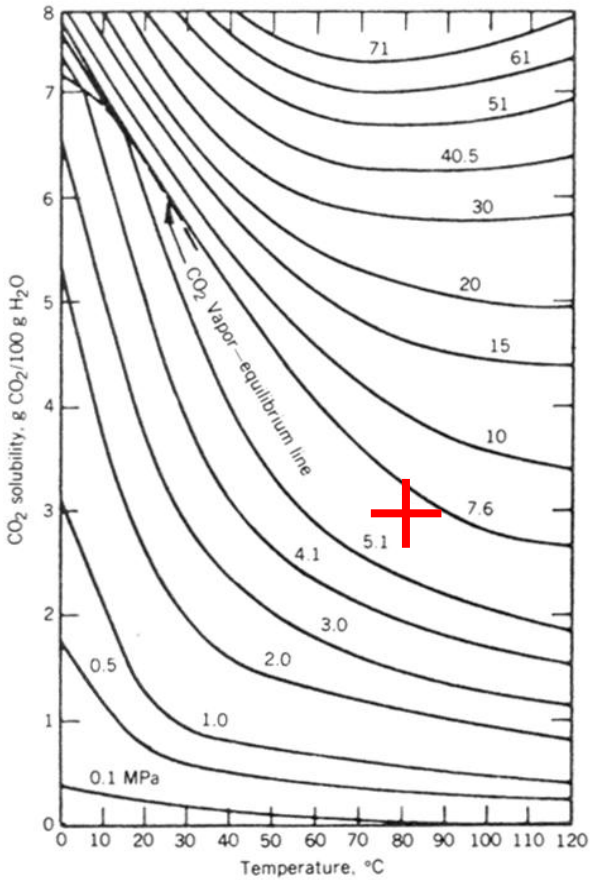
  - over 25% $MgCO_3$ in 30 min,
  - 22wt% total Mg in filtrate

$MgCO_3$ $3H_2O$

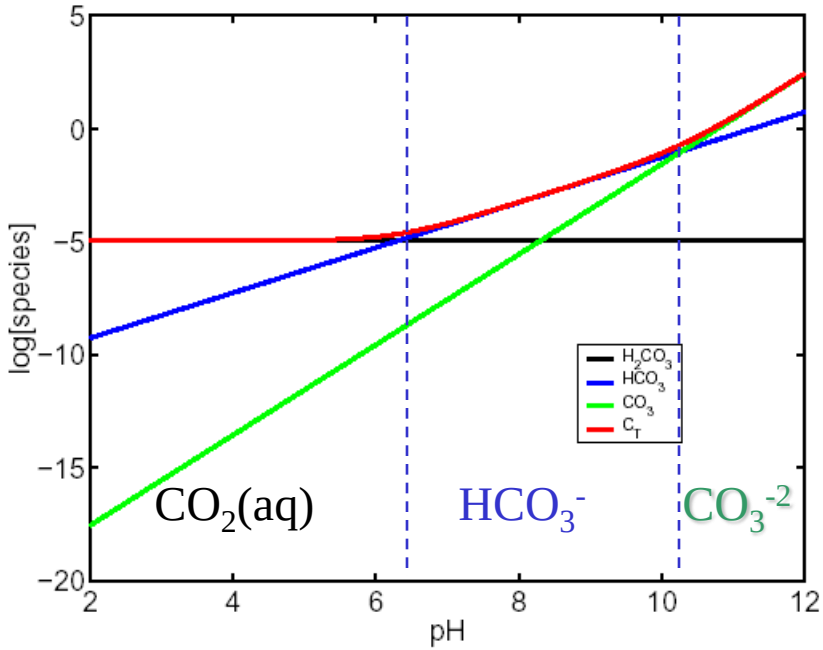


- Most of Fe remained as Fe(II) ion

Aqueous Carbonation Studies



(Pierantozzi, 1991)



- Solvent#7: 700 μg/mL → 0.029 M Mg^{2+}
- 3g CO_2 in 100g H_2O → 0.68 M
- At pH = 2, $[CO_3^{2-}] = 2.53 \times 10^{-6}$ M
- $[Mg^{2+}] >> [CO_3^{2-}]$

pH swing

(Park and Fan, Patent publication # 20050180910)

Grind Serpentine

Serpentine + Acid + chelating agent at higher T

pH 2 → SiO_2

Mg- and Fe-rich solution at room T

pH 8.6 → Precipitated iron oxide

High P
CO_2 (SO_2)

Mg-rich solution at room T

pH 9.5 → Precipitated $MgCO_3$

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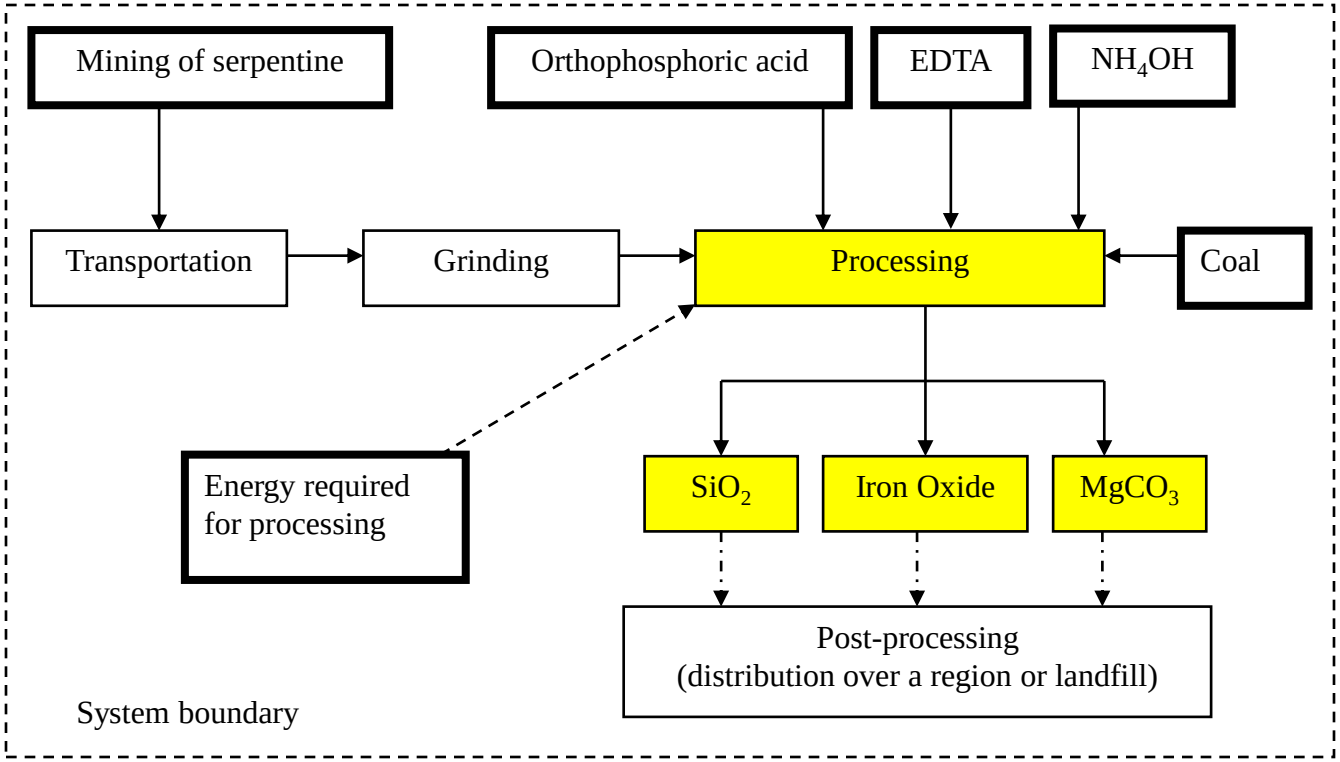
Life Cycle Assessment



Potential Usages of PMC & PCC

- PCC (precipitated $CaCO_3$)

  (Overall demand for PCC in USA was 7.75 MT in 2004)

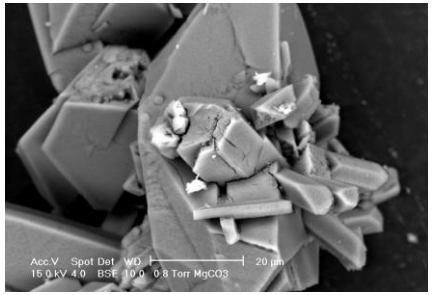
  – Crude $CaCO_3$ can be found in nature (limestone, seashells)

  – Increased demand from the paper industry since the mid-1980s: acid → neutral papermaking, replace kaolin

Market for $CaCO_3$ **PCC**

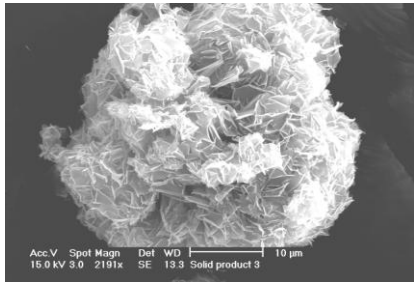
Industry	Consumption [%]
Paper	72
Paints	8
Plastics/Rubber	9.5
Other	10.5

Potential Usages of PMC

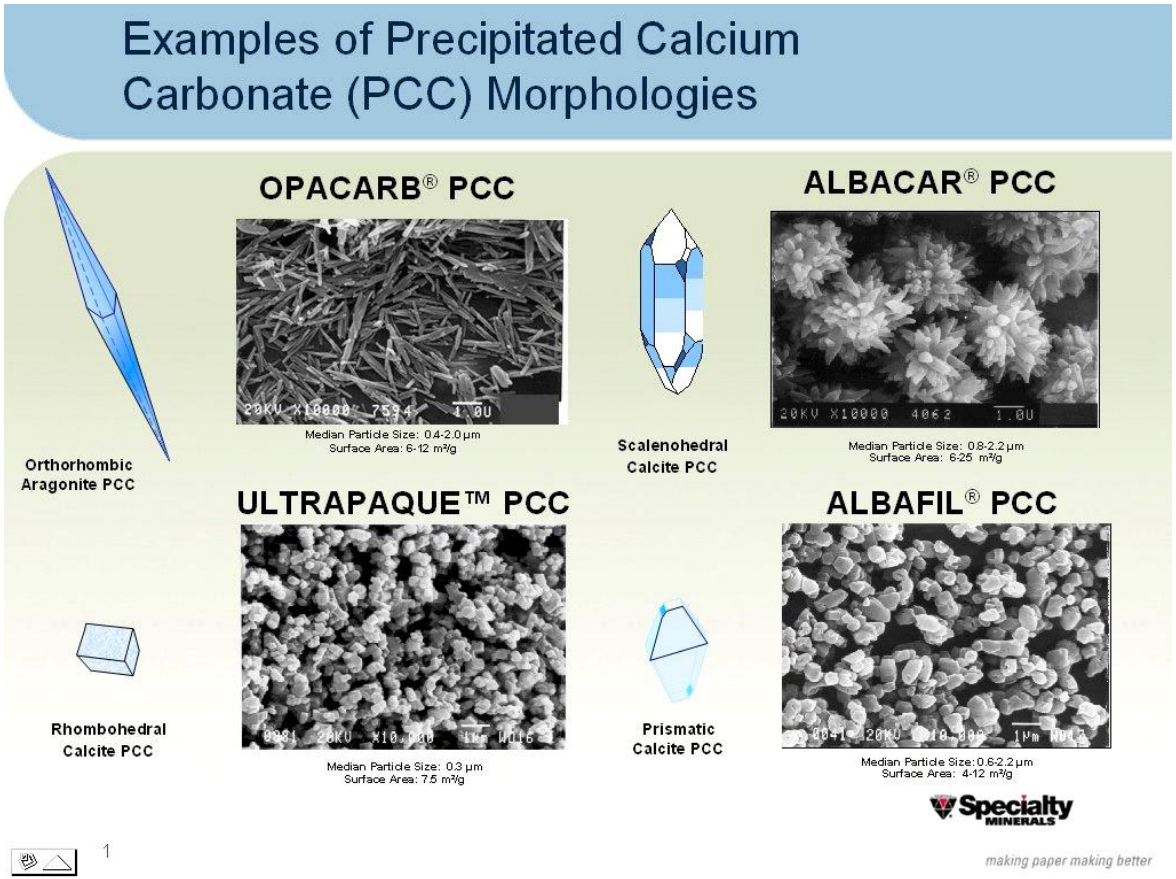


PMC w/o chelating agents

Vs.



PMC w/ chelating agents



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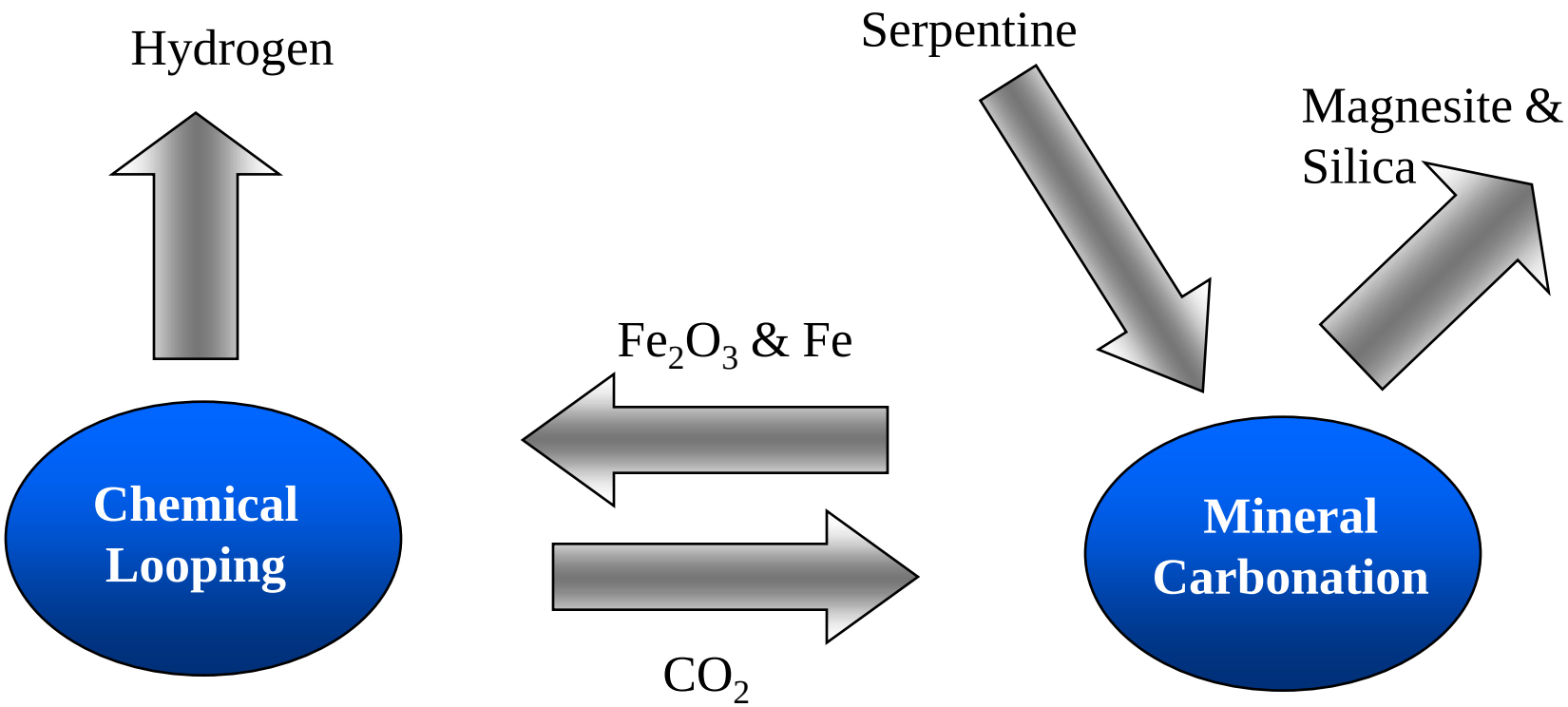
Potential Usages of Iron



Conclusions

- Fast dissolution of *serpentine* is achieved in a solvent made of weak acids and chelating agents, with in-situ physical activation.
- pH swing process allows carbon sequestration while generating value-added solid products – improves the overall economic feasibility of the carbon mineral sequestration technology.
- LCA provides a new parameter for the process optimization and estimates the actual amount of carbon sequestered.

Thank you