Chemical and Biological Catalytic Enhancement of Weathering of Silicate Minerals as Novel Carbon Capture and Storage Technology

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Element 1: Chemically Enhanced Mineral Dissolution

Goal: Enhance dissolution rate of magnesium containing serpentine mineral

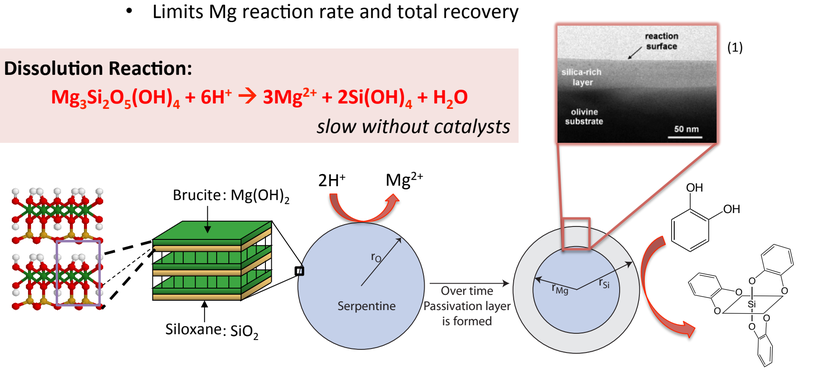
Challenge: While magnesium reacts quickly, a passivation layer of silica develops over time

- Limits Mg reaction rate and total recovery

Dissolution Reaction:

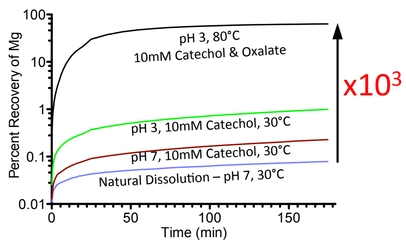
$Mg_3Si_2O_5(OH)_4 + 6H^+ \rightarrow 3Mg^{2+} + 2Si(OH)_4 + H_2O$

slow without catalysts



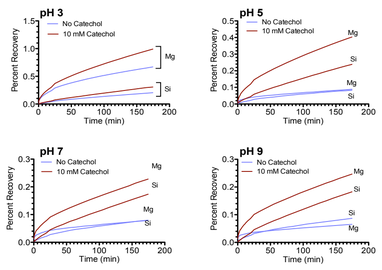
Silica can be removed catalytically
→ *Enhanced Mg reaction rate*
→ *Increased total recovery*

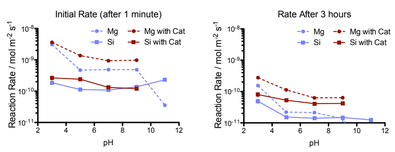
Material	Lizardite		
Solution	pH 7, Baseline	pH3, 1E-2 Cat & Ox	
Temp	30	80	
Time	Surface Rates (mol m^{-2} s^{-1})		Increase
0-4 min	6.80E-10	8.4E-08	124 x
4-20 min	7.00E-11	9.1E-08	1301 x
20-180 min	2.10E-11	2.2E-08	1041 x



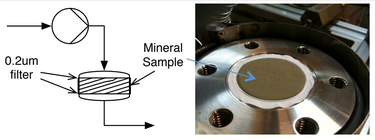
- *Increase in reaction rate sustained for > 3 hours*
- *> 60% Magnesium recovered*

Catalytic Silica removal consistently increases rates over a wide pH range:
→ *Allows for flexible process options*





- *Kinetics are measured in a custom designed Continuous-Flow Differential Bed Reactor*
- *Maintains constant solution condition for reproducible dissolution*



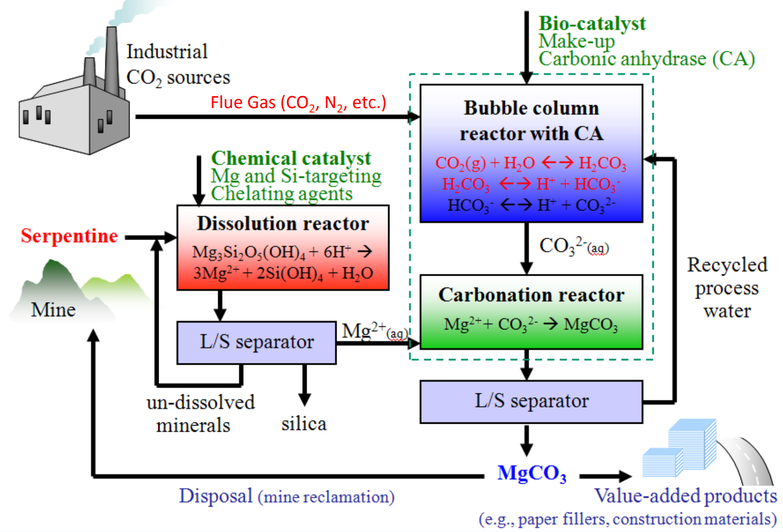
(1) Bearat et al. Carbon sequestration via aqueous olivine mineral carbonation: Role of passivating layer formation. Environ Sci Technol (2006) vol. 40 (15) pp. 4802-4808

Project Overview

Overall Mineral Weathering Reaction

$$3CO_2 + Mg_3Si_2O_5(OH)_4 \longrightarrow 3MgCO_3 + 2SiO_2 + 2H_2O$$

Proposed engineered mineral weathering process



Why Combine Carbon Capture and Storage?

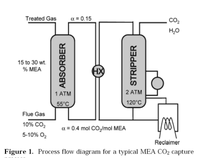
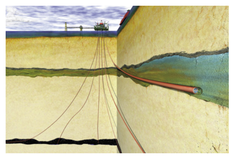
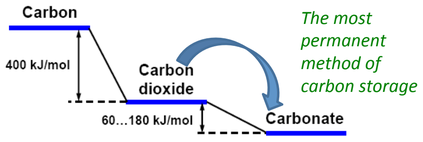


Figure 1. Process flow diagram for a typical MEA CO_2 capture process.

(Goff et al., *Ind. Eng. Chem. Res.* 2004)

Conventional CO_2 capture + Geologic storage scheme





- A single process that combines CO_2 capture and storage
  → No need for energy intensive solvent regeneration process
- The final product is thermodynamically stable solid mineral carbonates → No need for long term monitoring

Widely available Mg-bearing silicate minerals often located near power plants

Element 2: Bio-Catalyst Development

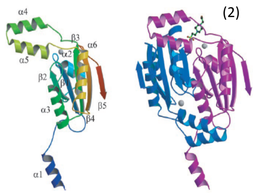
Goal: Develop a heterogeneous whole-cell biocatalyst based on carbonic anhydrase to increase the rate of CO_2 hydration in the aqueous phase

Hydration of Carbon Dioxide:

$CO_2(g) + H_2O \leftrightarrow H_2CO_3$
$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$ } *slow without catalysts*
$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$

Catalysis by Carbonic Anhydrase:

$EZnOH^- + CO_2 \leftrightarrow EZn(OH^-)CO_2 \leftrightarrow EZnHCO_3^- \leftrightarrow EZnH_2O + HCO_3^-$
$EZnH_2O \leftrightarrow EZnOH^- + H^+$

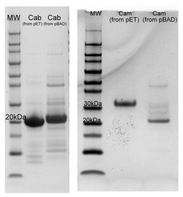


Cam (carbonic anhydrase methanosarcina)
- *Methanosarcina thermophila*
- Advantages:
  - Expressed in periplasm
  - High wild-type activity
- Areas for Development:
  - Limited thermostability
  - Trimeric
  - Anchoring and immobilization

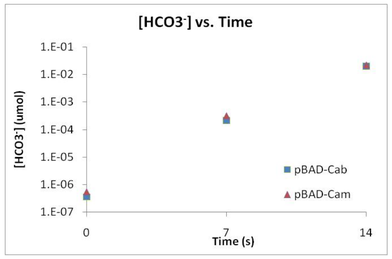
Cab (carbonic anhydrase beta)
- *Methanobacterium thermoautotrophicum*
- Advantages:
  - Thermostable
  - Relatively high wild-type activity
- Areas for Development:
  - Periplasmic expression
  - Dimeric and possibly tetrameric
  - Anchoring and immobilization

(1)

Two wild-type enzymes successfully cloned into cytoplasm and periplasm
→ *Activity confirmed in both vectors*

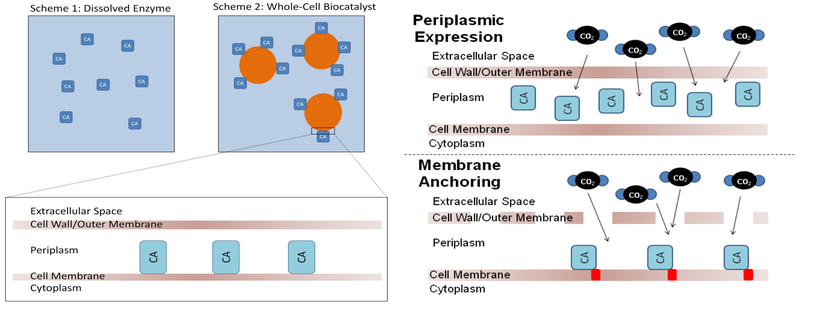


- *Periplasmic expression enables whole cells to be used as catalyst*
  → No need for expensive separation and purification
  → ease of separation



Purified enzymes can be replaced with whole cells

		#cells	Rate (umol/sec)	Rate/cell (umol/sec)	Equiv. n_BCA (umol)	Equiv. m_BCA (fg)
pBAD-Cab	2uL	2.0E+06	1.44E-03	7.2E-10	1.6E-13	4.9
pBAD-Cam	2uL	2.0E+06	1.56E-03	7.8E-10	1.8E-13	5.3



(1) Smith, K.S. and Ferry, J.G. "Prokaryotic carbonic anhydrases". FEMS Microbiology Reviews 24 (2000) 335-366.
(2) Strop, P., et. al. "Crystal structure of the "cab"-type b Class Carbonic Anhydrase from the Archaeon *Methanobacterium thermoautotrophicum*" J. Biol. Chem. 276 (2001) 10299-10305.