Vitamin C as a green high-performance CO_2 scrubber

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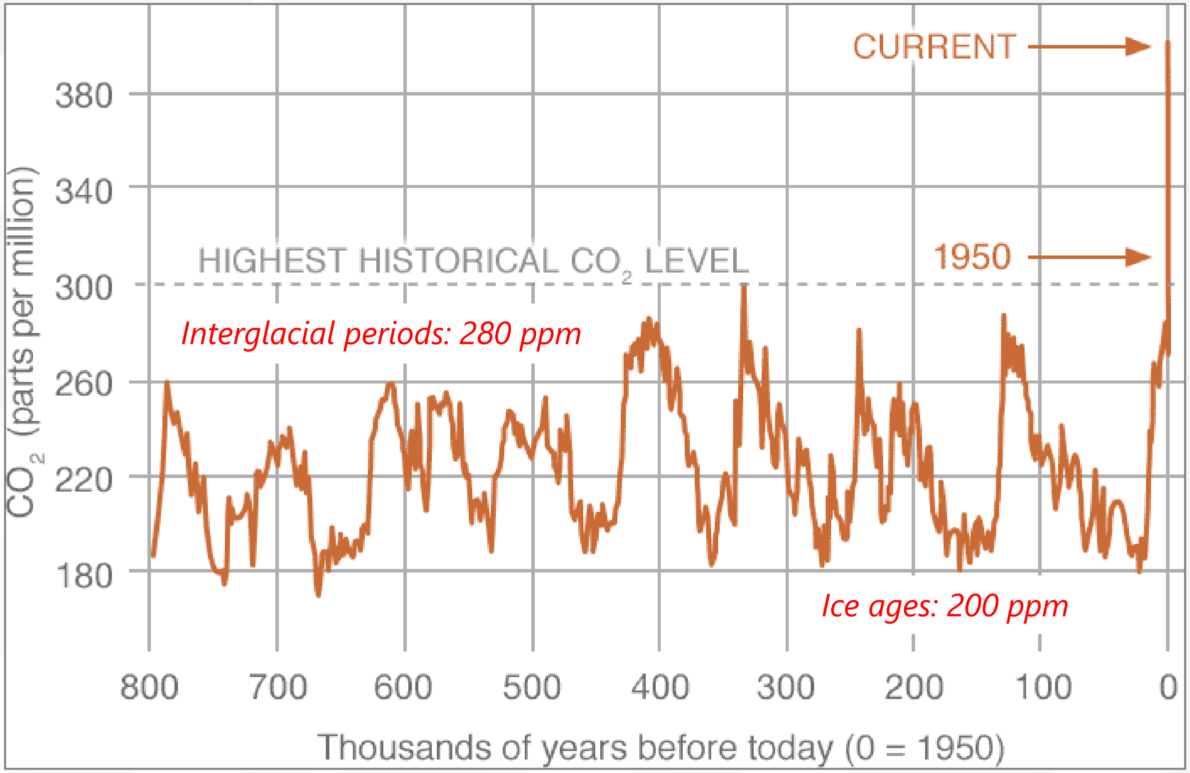
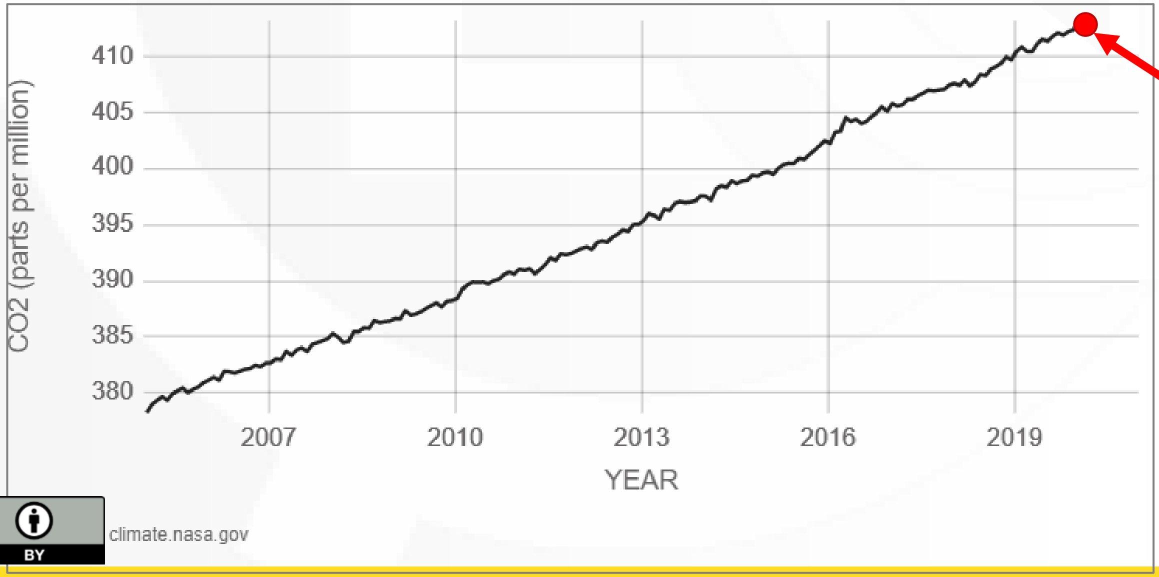
The relentless rise of carbon dioxide related to the fossil-fuel burning





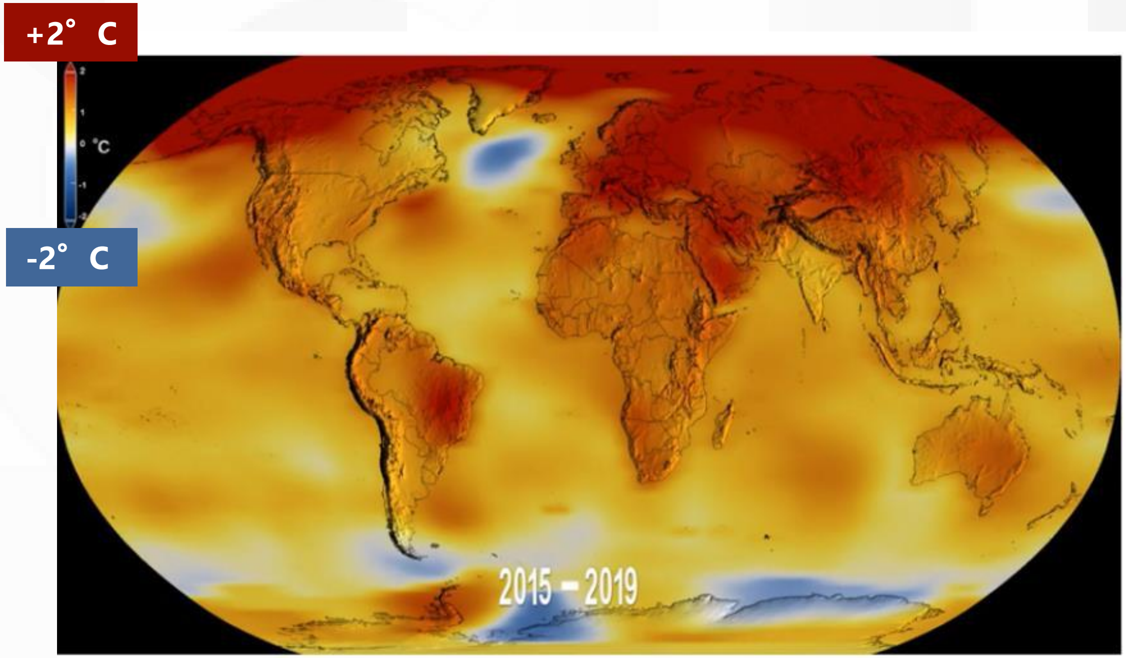
MARCH 17th, 2020
413,03 ppm

Data from climate.nasa.gov

CO_2 is the greenhouse gas most commonly produced by human activities and it is responsible for 64% of man-made global warming.

CO_2 rise effects:

- **Global Temperature Rise**
- **Oceans Warming**
- **Shrinking Ice Sheets**
- **Glacial Retreat**
- **Decreased Snow Cover**
- **Sea Level Rise**
- **Declining Arctic Sea Ice**
- **Extreme Events**
- **Ocean Acidification**



A PORTFOLIO OF SOLUTIONS is needed, among these **mineral trapping** → mainly involves **carbonates**

$MOH + \mathbf{CO_2} \rightarrow M(\mathbf{HCO_3})$

$MO + \mathbf{CO_2} \rightarrow \mathbf{MCO_3}$

$\mathbf{k_{sp}^{Cc} = 3.36 \times 10^{-9}}$

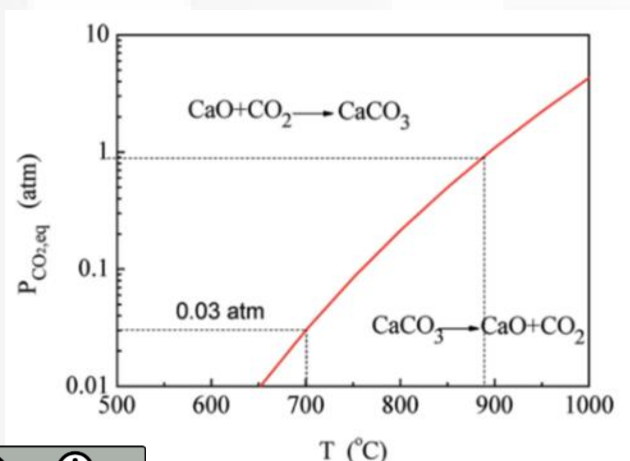
$\mathbf{k_{sp}^{Arag} = 6 \times 10^{-9}}$

S/V reactions

$CaCO_3 \Leftrightarrow Ca^{2+} + CO_3^{2-}$

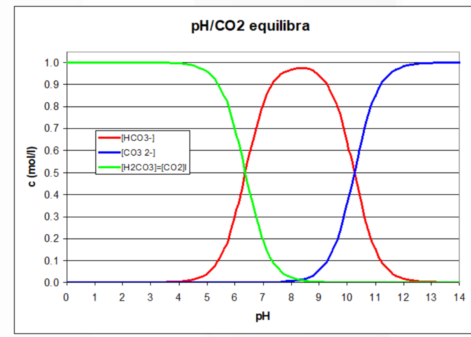
$CO_3^{2-} \Leftrightarrow [CO_2]_{ad} + O^{2-}$

$[CO_2]_{ad} \Leftrightarrow CO_2$



L/V reactions

$CO_2\ (g) \Leftrightarrow CO_2\ (l)$



$CO_2\ (l) + H_2O\ (l) \Leftrightarrow H_2CO_3\ (l)$

$H_2CO_3 + H_2O \Leftrightarrow H_3O+ + HCO^{3-}$ $pK_{\alpha 1}(25°\ C) = 6.37$

$HCO^{3-} + H_2O \Leftrightarrow H_3O+ + CO_3^{2-}$ $pK_{\alpha 2}\ (25°\ C) = 10.25$

$$CO_2(g) \Leftrightarrow CO_2(l) \overset{H_2O}{\Leftrightarrow} H_2CO_3 \overset{H_2O}{\Leftrightarrow} HCO_3^- + H_3O^+ \overset{H_2O}{\Leftrightarrow} CO_3^{2-} + H_3O^+ \overset{Ca^{2+}}{\Leftrightarrow} CaCO_3 \downarrow$$

Other methods:

C (IV) to C (III) reduction

- **Transition-metal complexes** are mandatory to direct the reactivity of the $CO_2^{\bullet-}$ radical anion towards a specific reaction product. Electrochemical parameters must be properly optimized.
- Photo-electrochemical and catalytical reduction of CO_2 are associated to a significant **energy drawback**.
- Reductive coupling of CO_2 to form oxalate has been accomplished by electrochemical reactions involving **transition metal** (Hg, Pb, Cu, Pd, Ag) **complexes** or **anion radicals of aromatic** hydrocarbons, esters, and nitriles

We proposed the C(IV) to C(III) reduction

via

Vitamin C

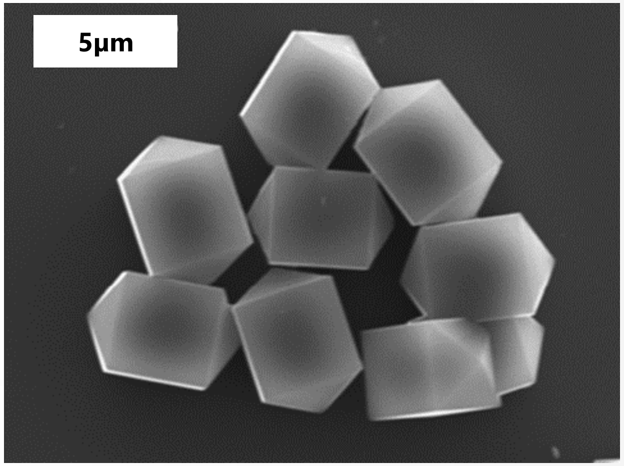
and carbon capture in stable calcium oxalates

$$2\mathbf{CO_2} + 2H^+ + 2e^- \rightarrow H_2\mathbf{C_2O_4}$$

$$\mathbf{AA} \rightarrow \mathbf{DHA'} + H^+ + e^-$$

$$\mathbf{Ca(ASC)_2} + \mathbf{2CO_2} + 2H^+ + 2e^- \rightarrow \mathbf{CaC_2O_4} + \mathbf{2DHA} + 2H^+ + 2e^-$$

$$\mathbf{k_{sp}^{COM} = 2.32 \times 10^{-9}}$$



facile, green and direct precipitation of calcium oxalates by carbon reduction using Vitamin C

Oxalate *VS* Carbonate

- $CO_2 \rightarrow C_2O_4^{2-}$

  Effective method for the CO_2 capture in a stable crystalline phase
  The reaction has been validated

- The capture efficiency is doubled with respect to carbonation

oxalate	*carbonate*
$CO_2/C_2O_4^{2-}$ =2:1	CO_2/CO_3= 1:1

- If dissolved, the CO_2 is not directly returned to the environment

Process behavior

The process happens following two steps:

1. The **red-ox** (reduction of CO_2 in $C_2O_4^{=}$ in the presence of Vitamin C).

   This is the *rate determining step* of the reaction → it must be promoted to reduce the induction time of the system. The variables playing a role here are mainly

   - *Competitors (O_2 for instance)*
   - *Temperature*
   - *pH*
   - *Reactive surface (aerosol)*

2. The **nucleation** of calcium oxalate.

   Very low k_{sp} → the nucleation is easily obtained

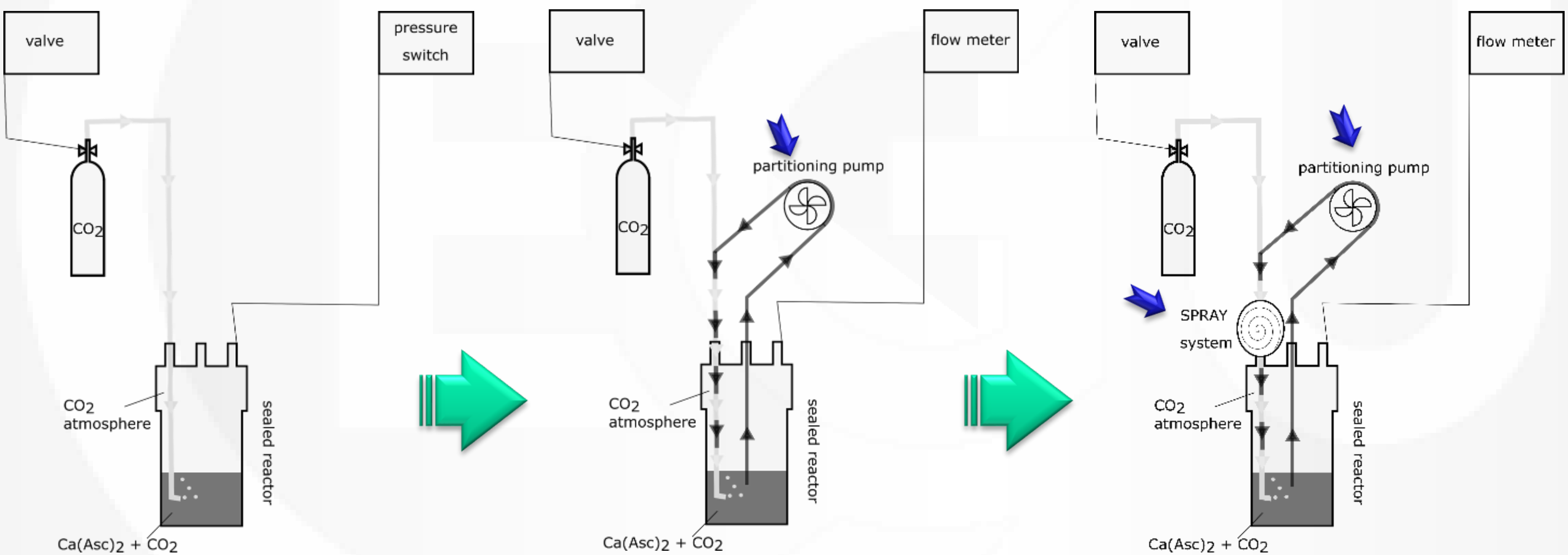
Reagents and products

Reducing agent: Vitamin C	Precipitate: Ca-oxalate mono/dihydrate
Not harmful	Not harmful
Easy to obtain (natural –from fruits and vegetables-; synthetic – from D-glucose-)	Stable solid phase, nearly negligible solubility
Reaction products (DHA, dehydroascorbic acid and following degradation cascade) not harmful	Inactive to the red-ox if left into the reaction vessel
Replaceable with other natural reducing agents potentially recovered from waste (circular approach)	Its degradation does not produce CO_2 (at temperature lower than 200° C)

Experimental setups

Many setups have been implemented:

- Air – **A** setup
- CO_2 saturated atmosphere (from $(NH_4)CO_3$ thermal decomposition) – **G** setup



- Bubbling CO_2 – **B** setup
- Bubbling CO_2 + microfluidic reactors – **BD** setup
- **Spray** setup

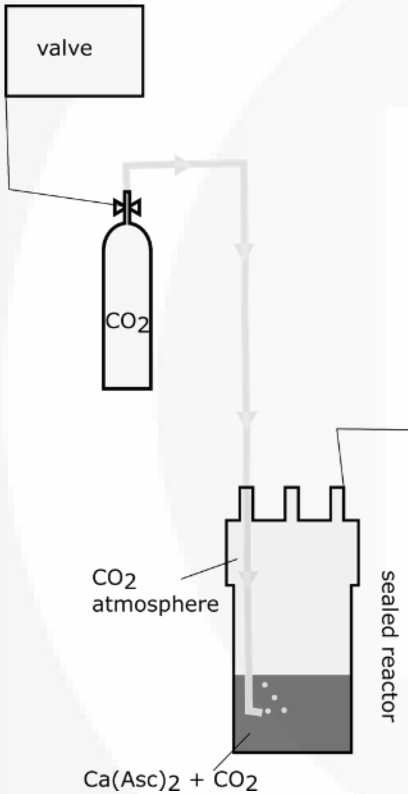
...optimizing the capture system...

Many variables have been tested and optimized on the B setup and then transferred to the more complexes BD and SPRAY setups:

- Stoichiometry (pH)
- Temperature
- Oxygen concentration
- Physical triggers (470 nm blue light)
- Solution «aging» time

Fluid fluxes have been tested directely on the BD and SPRAY setups.

...monitoring the CO_2 into the B reactor

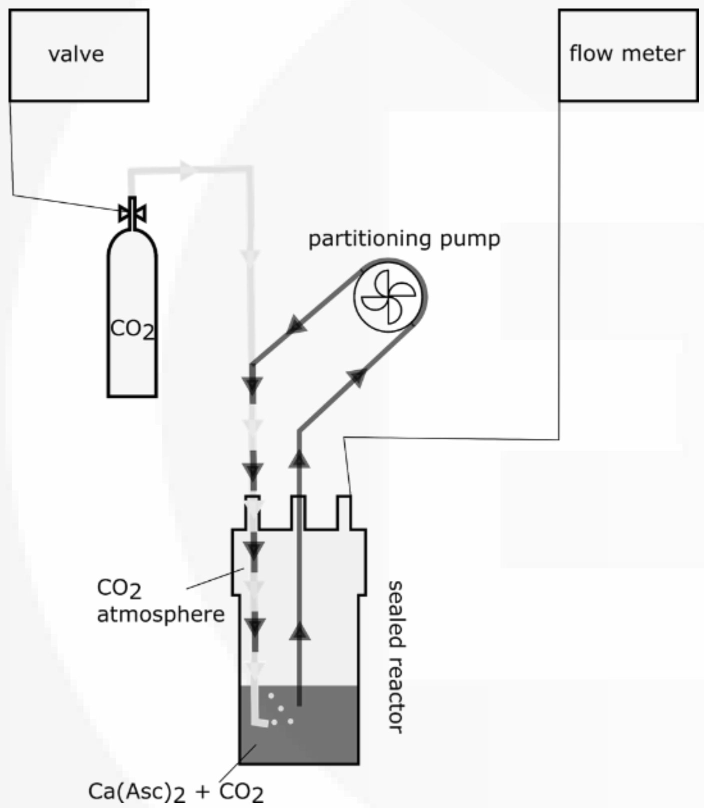


Pressure in a **sealed reactor** (**B setup**) decreases during the experiment

The pressure loss is directely related to the CO_2 consumption

Max capture efficiency ~ 10%

...monitoring the CO_2 into the BD reactor

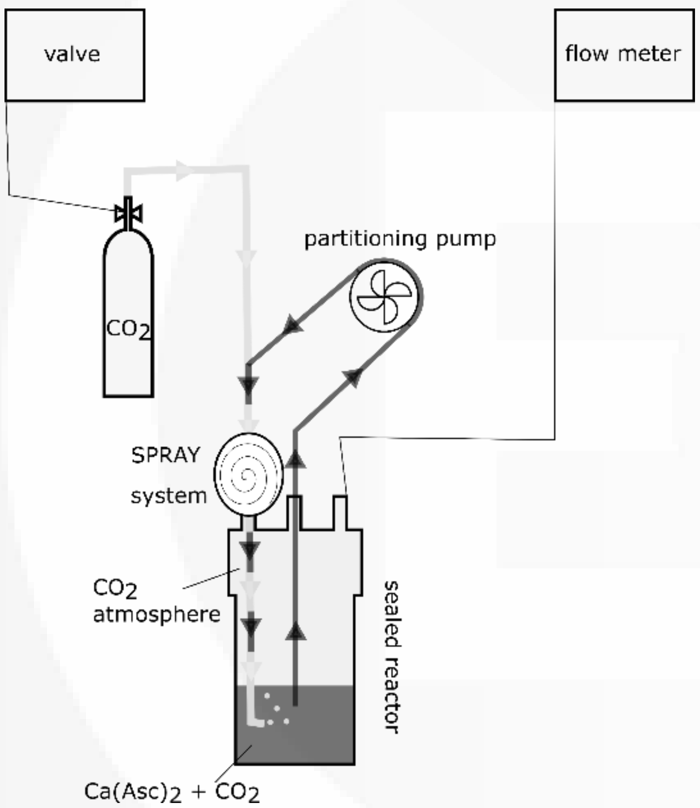


Flux fall at the outlet of a **fluxed reactor** (**BD setup**)

The flux loss is directely related to the CO_2 consumption

Max capture efficiency
~ 65%

…monitoring the CO_2 into the SPRAY reactor



Flux fall at the outlet of a **fluxed reactor** (**SPRAY setup**)

The flux loss is directely related to the CO_2 consumption

Max capture efficiency

~ 82%

A quantitative evaluation of the CO_2 trapping by carbon reduction via Vitamin C

Setup	Setup BD		Flux rate mL/min	Yield after 20 h (%)	
				Mix & work	Aging
B	Soichiometric solution (pH5.5)	no O_2	/	2	/
	Soichiometric solution (pH5.5)	Atmospheric O_2	/	3.75	6.25
	AA excess (pH5.3)	Atmospheric O_2	/	5.75	**9.5**
	Ca(OH)2 excess (pH5.8)	Atmospheric O_2	/	4.5	5
	Soichiometric solution (pH5.5)	H_2O_2 @ variable concentration	/	3-6.5	/
BD	AA excess (pH5.3)	Atmospheric O_2	1.25	/	**60.5**
SPRAY	AA excess (pH5.3)	Atmospheric O_2	1.25	/	**82**

Summarizing…

- A new green and easy to handle method for CCS has been proposed
- The reaction has been validated
- No harmful reagents and products involved

- The maximum yield (CO_2 captured) obtained till now → 82%

- The reaction yield depends on the reaction surface and on:
  - presence of O_2
  - mixing rate,
  - stoichiometry,
  - pH
  - temperature play a minor role on the performance of the system.

- For a circular approach, the reducing agent could be substituted by vitamin blends from the organic waste leachate

European Geosciences Union

Thank you for your attention!

Crystals Special Issue "***Crystal Growth in Environmental Protection, Remediation, and Health***"

Guest Editor **Dr. Linda Pastero**

Submission deadline: **30 June 2020**