

## Enzyme-accelerated CO<sub>2</sub> capture and storage (CCS) using paper and pulp residues as co-sequestering agents

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### Supporting information

#### 1. Calculations for CO<sub>2</sub> capture step

This study considered the main paths for the bicarbonate formation: the CO<sub>2</sub> hydration, and the mineral dissolution of CaCO<sub>3</sub>, Mg(OH)<sub>2</sub> and Ca(OH)<sub>2</sub>. The possible influence of other materials as CO<sub>2</sub> co-sequestering agents was not considered in this study scope. The carbon balance was performed according to the presence of the materials as presented in Table S1.

Table S1: Reactions for CO<sub>2</sub> capture for each evaluated residue

	CO <sub>2</sub> hydration	CaCO <sub>3</sub> dissolution	Mg(OH) <sub>2</sub> dissolution	Ca(OH) <sub>2</sub> dissolution
R1	Yes	Yes	No	No
R2	Yes	Yes	Yes	No
R3	Yes	Yes	No	No
R4	Yes	Yes	No	Yes

Reactions considered to contribute to CO<sub>2</sub> capture:

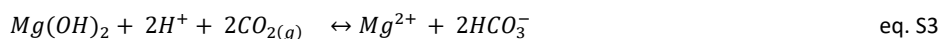
#### CO<sub>2</sub> hydration:



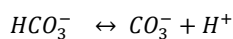
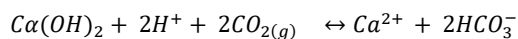
#### CaCO<sub>3</sub> dissolution:



#### Mg(OH)<sub>2</sub> dissolution:



**Ca(OH)<sub>2</sub> dissolution or Ca<sup>2+</sup> precipitation** (For pH>8, bicarbonate converts to carbonate that precipitates to CaCO<sub>3</sub>):



The total molar concentration of bicarbonate (HCO<sub>3</sub><sup>-</sup>) in the solution at end point:

$$[HCO_{3, \text{mineralization method}}^-] = [HCO_{3, CO_2 \text{ hydration}}^-] + [HCO_{3, CaCO_3 \text{ dissolution}}^-] + [HCO_{3, Mg(OH)_2 \text{ dissolution}}^-]$$

From eq. S2:

$$[HCO_{3, CaCO_3 \text{ dissolution}}^-] = \Delta [Ca^{2+}] = [Ca_t^{2+}] - [Ca_{t=0}^{2+}] > 0 \quad \text{eq. S5}$$

From eq. S3:

$$\left[ \text{HCO}_3^-, \text{Mg(OH)}_2, \text{dissolution} \right] = \frac{\Delta[\text{Mg}^{2+}]}{2} = \frac{[\text{Mg}_t^{2+}] - [\text{Mg}_{t=0}^{2+}]}{2} \quad (\text{From eq. S3}) \quad \text{eq. S6}$$

Thus:

$$\left[ \text{HCO}_3^-, \text{CO}_2 \text{ hydration} \right] = \left[ \text{HCO}_3^-, \text{mineralization method} \right] - \left[ \text{HCO}_3^-, \text{CaCO}_3, \text{dissolution} \right] - \left[ \text{HCO}_3^-, \text{Mg(OH)}_2, \text{dissolution} \right] \quad \text{eq. S7}$$

From eq. S4:

$$\left[ \text{HCO}_3^-, \text{Ca(OH)}_2, \text{dissolution} \right] = \left[ \text{CO}_3^{2-}, \text{Ca(OH)}_2, \text{dissolution} \right] = \frac{\Delta[\text{Ca}^{2+}]}{2} = \frac{[\text{Ca}_t^{2+}] - [\text{Ca}_{t=0}^{2+}]}{2} < 0 \quad \text{eq. S8}$$

Finally, the total molar concentration of CO<sub>2</sub> capture in bicarbonate equivalent is:

$$\left[ \text{HCO}_3^-, \text{total} \right] = \left[ \text{HCO}_3^-, \text{mineralization method} \right] + \left[ \text{HCO}_3^-, \text{Ca(OH)}_2, \text{dissolution} \right] = \left[ \text{CO}_2, \text{total} \right] \quad \text{eq. S9}$$

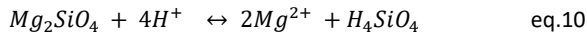
The concentration of CO<sub>2</sub> captured (g/L):

$$C = \frac{[\text{HCO}_3^-] \cdot 44}{61}$$

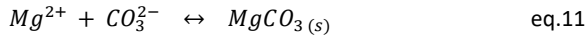
## 2. Calculations for CO<sub>2</sub> storage step

Reactions considered to contribute to CO<sub>2</sub> storage:

**Mineral dissolution:**



**Mineral carbonation:**



The solution used as source of bicarbonate (HCO<sub>3</sub><sup>-</sup>) from the CO<sub>2</sub> capture step contains Mg<sup>2+</sup> and Ca<sup>2+</sup>.

The concentration of Mg<sup>+2</sup> ions leached during the olivine dissolution is calculated as:

$$\left[ \text{Mg}_{\text{olivine dissolution}}^{2+} \right] = \Delta[\text{Mg}^{2+}] = [\text{Mg}_t^{2+}] - [\text{Mg}_{t=0}^{2+}] = [\text{Mg}_t^{2+}] - \left[ \text{Mg}_{\text{CO}_2 \text{ capture}}^{2+} \right] \quad \text{eq. S10}$$

The concentration of Ca<sup>+2</sup> ions was proven to decrease over time during olivine dissolution, forming insoluble salts.

The yield of mineral carbonation can be calculated considering only formation of MgCO<sub>3</sub>, as Mg is mainly the element that derives from the olivine mineral during dissolution. Mg<sup>+2</sup> is the limiting reactant, according to tested conditions: 1 g/L HCO<sub>3</sub><sup>-</sup>= 0.016 mol/L and max 154 mg/L Mg<sup>+2</sup>=0.00625 mol/L. From eq. S11:

$$\text{Carbonation yield}\% = - \frac{[\text{Mg}_t^{2+}] - [\text{Mg}_{t=0}^{2+}]}{[\text{Mg}_{t=0}^{2+}]} \cdot 100 = - \frac{[\text{Mg}_t^{2+}] - [\text{Mg}_{\text{olivine dissolution}}^{2+}]}{[\text{Mg}_{\text{olivine dissolution}}^{2+}]} \cdot 100 \quad \text{eq. S11}$$

## 3. Mass balance XRD and XRF

For estimating the concentration of the main phases in the studied residues a mass balance was performed comparing the data obtained from XRF and XRD analysis. The first was utilized to calculate the elements concentration and the latter the main phases found in the residue. Some simplifications were done during the mass balance, which are:

- 1) Elements found with concentration lower than 0.3% (XRF) were not considered in mass balance of the phase's concentration determination.
- 2) The concentration of each phase was tested to "close" the element mass balance:
  - a.  $\% \text{Total Element}_{\text{XRF}} = \sum_i^n \% \text{Element}_{\text{phase}_{i,\text{XRD}}} = \sum_i^n (\% \text{Phase}_{i,\text{XRD}} \times \text{MM}_{\text{element}} / \text{MM}_{\text{phase},i})$ .
  - b. The elements not considered in the mass balance (%w < 0.3) were assumed to belong to other phases .
  - c.  $\sum_i^n \% \text{Phase}_{i,\text{XRD}} \sim 100.00\% ((\sum_i^n \% \text{Phase}_{i,\text{XRD}} - 100\%) / 100\% < 1.0\%)$ .

Where:

$\%Element_{XRF}$  is the percentage (in %w) measured in XRF analysis.

$\%Phase_{i,XRD}$  is the attributed percentage (in %w) of the phase.

In table S2, an example of the how the final mass balance of a residue would look like.

Table S2: Example of mass balance for a reference material.

Phase/Element	% phase	Ca	Mg	C	O	Al	H	Fe
CaCO <sub>3</sub> (Calcite)	$\%Phase_{CaCO_3,XRD}$	$\%Element_{phase_{CaCO_3,XRD}}$	...				...	
Mg(OH) <sub>2</sub>	...	...						
CaO								
Kieserite (MgSO <sub>5</sub> H <sub>2</sub> )								
Almandine (Fe <sub>3</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>12</sub> )								
Other phases	$\%Phase_{other\ phases}$	...						
<b>Total</b>	100	$\%Ca_{XRF}$	...					$\%Fe_{XRF}$

#### 4. XRD analysis – Olivine before and after the CO<sub>2</sub> storage reaction

Olivine prior and after the dissolution/mineral carbonation (in presence of bicarbonate from no CA-added CO<sub>2</sub> capture reaction and bicarbonate from a CA-added CO<sub>2</sub> capture reaction) were analyzed. Results did not point significant changes between the samples before and after reaction.

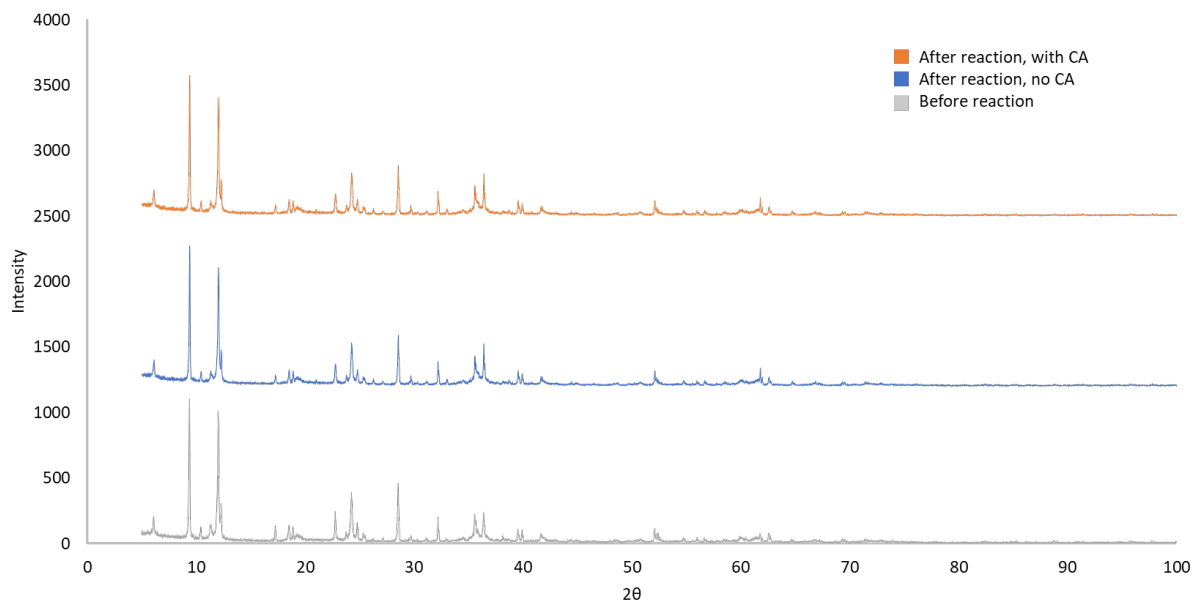


Figure S1: XRD spectra of olivine - before and after reaction

## 5. TGA – Olivine before and after reaction the CO<sub>2</sub> storage reaction

TGA analysis showed that the olivine after reaction (using bicarbonate from no CA-added CO<sub>2</sub> capture reaction and using bicarbonate from a CA-added CO<sub>2</sub> capture reaction) presented higher mass loss when compared to the unreacted mineral. Some moisture was identified, corresponding to the mass loss between 30-130°C. Between 500-900°C the mass loss for all materials was 74.5-75.4%, indicating the presence of CaCO<sub>3</sub>. Between 300-350°C, both no- and CA added systems presented a slight difference (around 0.9%) in mass decrease when compared to non-reacted olivine – which could be due the formation of nesquehonite (MgCO<sub>3</sub>·3H<sub>2</sub>O), as showed in S4.

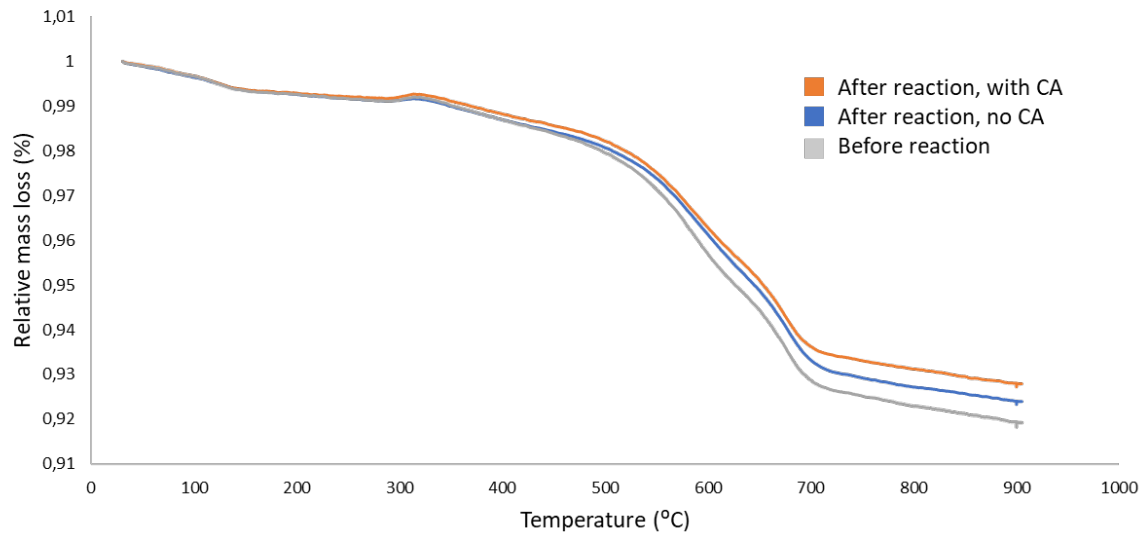


Figure S2: TGA of olivine before and after reaction