

Supporting information for

Electrolytic Mineralization of CO₂

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Supplementary Calculations.

For this section, we provide the reader with a glossary of terms and variables (Supplementary Table 1).

Supplementary Table 1: Glossary of terms and variables used to express metrics in this study.

Variable	Symbol	Meaning
Calcium transference efficiency	$\eta_{Ca, transfer}$	$\eta_{Ca, transfer} = n_{Ca^{2+}, catholyte} / n_{Ca^{2+}, chemolyte} \times 100\%$ <p>Ratio of mol $Ca^{2+}_{(aq)}$ ions in the catholyte, $n_{Ca^{2+}, catholyte}$, to mol Ca^{2+} liberated from silicates (e.g., $CaSiO_3$) in the chemical chamber, $n_{Ca^{2+}, chemolyte}$, times 100%.</p>
Calcium carbonation efficiency	$\eta_{Ca, carbonation}$	$\eta_{Ca, carbonation} = n_{CaCO_3} / n_{Ca^{2+}, chemolyte} \times 100\%$ <p>Ratio of number of moles of $CaCO_3$ that precipitated in the cathode chamber after electrolysis, n_{CaCO_3} to $n_{Ca^{2+}, chemolyte}$, times 100%.</p>
CO ₂ mineralization efficiency	$\eta_{mineralization}$	$\eta_{mineralization} = n_{CaCO_3} / n_{CO_2} \times 100\%$ <p>Ratio between moles of $CaCO_3$ that precipitated in the cathode chamber after electrolysis (n_{CaCO_3}), and the total moles of CO₂ purged into the cathode chamber during electrolysis (n_{CO_2})</p>
CO ₂ mineralization rate	r	<p>Tons of mineralized CO₂ per tons of silicate minerals per year, where r_{CaSiO_3} represents wollastonite ($CaSiO_3$), $r_{Mg_2SiO_4}$ represents forsterite (Mg_2SiO_4).</p>

	$n_{Ca^{2+}, chemolyte}$	Moles of soluble Ca^{2+} in the chemolyte sourced from solid $CaSiO_3$.
	n_{CaCO_3}	Moles of $CaCO_3$ that precipitated in the cathode chamber after electrolysis. This white solid is primarily $CaCO_3$, but may contain trace quantities of $Ca(OH)_2$.
	$n_{Ca^{2+}, catholyte}$	Moles of soluble $Ca^{2+}_{(aq)}$ ions in the catholyte.
	n_e^-	Moles of electrons used for electrolysis.
	n_{CO_2}	Moles of CO_2 purged into the catholyte during electrolysis.
	m_{CaCO_3}	Mass of $CaCO_3$ precipitated in the cathode chamber.
	m_{CO_2}	Mass of CO_2 captured and converted into $CaCO_3$ in the weathering electrolyzer.
	m_{CaSiO_3}	Mass of $CaSiO_3$ dissolved in the chemical chamber during electrolysis.
	$V_{catholyte}$	Volume of catholyte for calcium transference efficiency determination test (i.e., 0.5 L).
	V_{CO_2}	Total volume of CO_2 purged into the catholyte during electrolysis.
	V_m	Molar volume at operating temperature (24.055 L mol ⁻¹ at 20 °C).
	t	Duration of electrolysis (i.e., 1 hour).
	t_W	Duration of weathering (i.e., 1 yr)
	$[Ca^{2+}_{(aq)}]_{chemolyte}$	Ca^{2+} concentration in the chemolyte at any point in time during electrolysis.
	$[Ca^{2+}_{(aq)}]_{catholyte}$	Ca^{2+} concentration in the catholyte at any point in time during electrolysis.

	F	Faraday constant: 96485 C mol^{-1} , where $C = \text{A} \cdot \text{s}$.
	i	Applied current density (i.e., 0.1 A cm^{-2}).
	k	Slope of $[\text{Ca}^{2+}_{(\text{aq})}]$ versus time (see Fig. 2B).
	Q	Flow rate of gas
	SA	Geometric surface area of electrodes (i.e., 4 cm^2).
	χ_{CO_2}	Molar fraction of CO_2 in the purged gas.

Calcium transference efficiency ($\eta_{Ca, transfer}$)

We set out to quantify the amount of Ca^{2+} liberated from the silicate that passed through the Ca^{2+} -exchanged CEM into the catholyte. We define this term as the “calcium transference efficiency” ($\eta_{Ca, transfer}$).

$$\eta_{Ca, transfer} = \frac{n_{Ca^{2+}, catholyte}}{n_{Ca^{2+}, chemolyte}} \times 100\%$$

where $n_{Ca^{2+}, catholyte}$ was measured by ICP-OES, and it was determined indirectly from the Ca^{2+} concentration in the catholyte at any point in time during electrolysis (Fig. 2). The $n_{Ca^{2+}, chemolyte}$ was calculated based on the number of moles of electrons used for electrolysis (n_{e^-}) and Faraday's law.

$$n_{Ca^{2+}, catholyte} = [Ca_{(aq)}^{2+}]_{catholyte} \cdot V_{catholyte}$$

$$n_{Ca^{2+}, chemolyte} = \frac{n_{e^-}}{N} = \frac{it}{NF} SA$$

$$n_{Ca^{2+}, chemolyte} = \frac{n_{e^-}}{N} = \frac{iAt/F}{N}$$

where, i is the applied current density (i.e., 100 mA cm⁻²); SA is the geometric surface area of electrodes (i.e. 4 cm²); t is the duration of electrolysis (i.e. 1 h); F is Faraday constant (96485 C mol⁻¹), N is the number of transferred electrons per dissolved Ca^{2+} (i.e., 2). The volume of catholyte for calcium transference efficiency determination test ($V_{catholyte}$, i.e. 0.5 L).

Substitution yields:

$$\eta_{Ca, transfer} = \frac{[Ca_{(aq)}^{2+}]_{catholyte}}{t} \frac{NFV_{catholyte}}{iSA} \times 100\%$$

The slope of $[Ca^{2+}]$ versus time in Fig. 2, k , was expressed:

$$k = \frac{[Ca_{(aq)}^{2+}]_{catholyte}}{t}$$

Thus, substitution yields:

$$\eta_{Ca, transfer} = k \frac{NFV_{catholyte}}{i SA} \times 100\%$$

Sample calculation:

The slope obtained from Fig. 2 is 0.246 mmol L⁻¹ min⁻¹, or 4.10 × 10⁻⁶ mol L⁻¹ s⁻¹ in SI units.

$$\begin{aligned} \eta_{Ca, transfer} &= k \frac{NFV_{catholyte}}{i SA} \times 100\% \\ &= 4.10 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1} \times \frac{0.5 \text{ L} \times 2 \times 96485 \text{ C mol}^{-1}}{0.1 \text{ A cm}^{-2} \times 4 \text{ cm}^2} \times 100\% \\ &= 4.10 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1} \times 2.41 \times 10^5 \frac{\text{L (A s) mol}^{-1}}{\text{A}} \times 100\% = 98.9\% \end{aligned}$$

This high calcium transference efficiency shows effectively quantitative permeance of dissolved Ca²⁺ through the Ca-CEM into the cathode chamber. We note that in order to determine $\eta_{Ca, transfer}$, we performed electrolysis without supplying any CO₂ supplied to the cathode, and ensured that all of the Ca²⁺ that passed through the membrane remained soluble in the catholyte by adding 20 mM of ethylenediaminetetracetic acid disodium (EDTA-2Na, Sigma Aldrich) the catholyte, and using a larger catholyte recirculating volume of 500 mL. During electrolysis, 2 mL of chemolyte and catholyte were taken out by a syringe at variable time periods and filtered with a member filter unit (Millipore, 0.22 μm). A volume of 1 mL of the filtered solutions were diluted with 3% nitric acid (10 times for catholyte and 100 times for chemolyte). The acidic dilute solutions were tested by inductively coupled plasma optical emission spectroscopy (ICP-OES) to determine [Ca²⁺_(aq)].

Calcium carbonation efficiency ($\eta_{Ca, carbonation}$)

We define the calcium carbonation efficiency ($\eta_{Ca, carbonation}$) as:

$$\eta_{Ca, carbonation} (\%) = \frac{n_{CaCO_3}}{n_{Ca^{2+}, chemolyte}} \times 100\%$$

where n_{CaCO_3} was calculated using the following equation.

$$n_{CaCO_3} = \frac{m_{CaCO_3}}{M_{CaCO_3}}$$

where m_{CaCO_3} is the mass of $CaCO_3$ that precipitated in the cathode chamber after electrolysis and M_{CaCO_3} is the molar mass of $CaCO_3$. Substitution yields:

$$\eta_{Ca, carbonation} (\%) = \frac{\frac{m_{CaCO_3}}{M_{CaCO_3}}}{\frac{it}{NF} SA} \times 100\% = \frac{NFm_{CaCO_3}}{it SA M_{CaCO_3}} \times 100\%$$

Sample calculation:

For example, when simulated flue gas was purged into the catholyte over 1 h of electrolysis, the obtained $CaCO_3$ in the cathode chamber was 0.4992 g. Thus, $\eta_{Ca, carbonation}$ can be calculated as follows:

$$\begin{aligned} \eta_{Ca, carbonation} (\%) &= \frac{NFm_{CaCO_3}}{it SA M_{CaCO_3}} \times 100\% \\ &= \frac{2 \times 96485 \text{ C mol}^{-1} \times 0.4992 \text{ g}}{0.1 \text{ A cm}^{-2} \times 4 \text{ cm}^2 \times 1 \text{ h} \times 100.09 \text{ g mol}^{-1}} = \frac{2 \times 96485 \text{ A s mol}^{-1} \times 0.4992 \text{ g}}{0.4 \text{ A} \times 3600 \text{ s} \times 100.09 \text{ g mol}^{-1}} \\ &= \frac{96330 \text{ A s g mol}^{-1}}{144130 \text{ A s g mol}^{-1}} \times 100\% = 67\% \end{aligned}$$

CO₂ mineralization efficiency ($\eta_{\text{mineralization}}$)

We define the CO₂ mineralization efficiency as:

$$\eta_{\text{mineralization}} (\%) = \frac{n_{\text{CaCO}_3}}{n_{\text{CO}_2}} \times 100\%$$

The n_{CO_2} is calculated on the basis of the total volume of CO₂ purged into the catholyte during electrolysis (V_{CO_2}) and the molar volume at operating temperature (V_m), which is calculated as 24.055 L mol⁻¹ at 20 °C.

$$n_{\text{CO}_2} = \frac{V_{\text{CO}_2}}{V_m} = \frac{\chi_{\text{CO}_2} Q t}{V_m}$$

where χ_{CO_2} is a molar fraction of CO₂ in the purged gas (i.e., 0.04% for air and 10% for flue gas); Q is the flow rate of gas. Substitution yields:

$$\eta_{\text{mineralization}} (\%) = \frac{m_{\text{CaCO}_3} V_m}{\chi_{\text{CO}_2} Q t M_{\text{CaCO}_3}} \times 100\%$$

Sample calculation:

For example, with 0.2 L min⁻¹ simulated flue gas (10% CO₂) flowing into catholyte, we collected 0.4992 g CaCO₃ in the cathode chamber and we calculated $\eta_{\text{mineralization}}$.

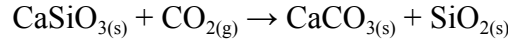
$$\begin{aligned} \eta_{\text{mineralization}} (\%) &= \frac{m_{\text{CaCO}_3} V_m}{\chi_{\text{CO}_2} Q t M_{\text{CaCO}_3}} \times 100\% \\ &= \frac{0.4992 \text{ g} \times 24.055 \text{ L mol}^{-1}}{10\% \times 0.2 \text{ L min}^{-1} \times 1 \text{ h} \times 100.09 \text{ g mol}^{-1}} = \frac{0.4992 \text{ g} \times 24.055 \text{ L mol}^{-1}}{10\% \times 0.2 \text{ L min}^{-1} \times 60 \text{ min} \times 100.09 \text{ g mol}^{-1}} \end{aligned}$$

$$= \frac{12.008 \text{ g L mol}^{-1}}{120.108 \text{ L g mol}^{-1}} \times 100\% = 10\%$$

CO₂ mineralization rate of natural rock weathering

It has been estimated that 0.127 Gt of CO₂ is removed annually by the natural weathering of silicates.¹ For this exercise, we assumed that all of this CO₂ is mineralized by a single silicate mineral, either wollastonite (CaSiO₃) or forsterite (Mg₂SiO₄). We can then express the CO₂ mineralization rate of natural weathering by the mass of CO₂ being mineralized to the mass of silicate minerals per year.

For example, the natural weathering of CaSiO₃ is expressed as.



Thus, the CO₂ mineralization rate of natural weathering with wollastonite (r_{CaSiO_3}) can be calculated as follows:

$$r_{\text{CaSiO}_3} = \frac{m_{\text{CO}_2, W}}{m_{\text{CaSiO}_3, W} t_W} = \frac{m_{\text{CO}_2, W}}{m_{\text{CO}_2, W} t_W \frac{N_{\text{CaSiO}_3/\text{CO}_2} M_{\text{CaSiO}_3}}{M_{\text{CO}_2}}} = \frac{M_{\text{CO}_2}}{M_{\text{CaSiO}_3} N_{\text{CaSiO}_3/\text{CO}_2} t_W}$$

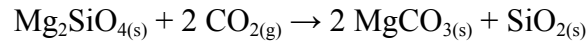
where $m_{\text{CO}_2, W}$ is the mass of CO₂ removed per year through natural weathering (0.127 Gt), $m_{\text{CaSiO}_3, W}$ is the mass of wollastonite needed to remove all this CO₂ through natural weathering (i.e., 0.335 Gt); t_W is the duration of weathering (i.e., 1 yr); M_{CO_2} and M_{CaSiO_3} are the molar masses of CO₂ (44.01 g mol⁻¹) and CaSiO₃ (116.16 g mol⁻¹), respectively; $N_{\text{CaSiO}_3/\text{CO}_2}$ is the stoichiometric ratio of Ca to CO₂ (i.e., 1).

Using these assumptions, the CO₂ mineralization rate of natural weathering with wollastonite is estimated as follows:

$$r_{CaSiO_3} = \frac{M_{CO_2}}{M_{CaSiO_3} N_{CaSiO_3/CO_2} t_W} = \frac{44.01 \text{ g mol}^{-1}}{116.16 \text{ g mol}^{-1} \times 1 \times 1 \text{ yr}}$$

$$= 0.379 \text{ g}_{CO_2} \text{ g}_{CaSiO_3}^{-1} \text{ yr}^{-1} = 0.379 \text{ ton}_{CO_2} \text{ ton}_{CaSiO_3}^{-1} \text{ yr}^{-1}$$

The same procedure can be used to estimate the CO₂ mineralization rate of natural weathering with forsterite ($r_{Mg_2SiO_4}$).



$$r_{Mg_2SiO_4} = \frac{m_{CO_2, W}}{m_{Mg_2SiO_4, W} t_W} = \frac{m_{CO_2, W}}{m_{CO_2, W} \frac{N_{Mg_2SiO_4/CO_2} M_{Mg_2SiO_4}}{M_{CO_2}}} = \frac{M_{CO_2}}{M_{Mg_2SiO_4} N_{Mg_2SiO_4/CO_2} t_W}$$

where $m_{Mg_2SiO_4, W}$ is the mass of forsterite needed to remove all this CO₂ through natural weathering, i.e. 0.203 Gt; $M_{Mg_2SiO_4}$ the molar mass of Mg₂SiO₄ (140.69 g mol⁻¹); $N_{Mg_2SiO_4/CO_2}$ is the stoichiometric ratio of Mg₂SiO₄ to CO₂ (i.e., 0.5).

Using these assumptions, $r_{Mg_2SiO_4}$ is estimated as follows:

$$r_{Mg_2SiO_4} = \frac{M_{CO_2}}{M_{Mg_2SiO_4} N_{Mg_2SiO_4/CO_2} t_W} = \frac{44.01 \text{ g mol}^{-1}}{140.69 \text{ g mol}^{-1} \times 0.5 \times 1 \text{ yr}}$$

$$= 0.626 \text{ g}_{CO_2} \text{ g}_{Mg_2SiO_4}^{-1} \text{ yr}^{-1} = 0.626 \text{ ton}_{CO_2} \text{ ton}_{Mg_2SiO_4}^{-1} \text{ yr}^{-1}$$

CO₂ mineralization rate of weathering electrolyzer

Our study centered on CaSiO₃, and thus the weathering reaction for wollastonite was used to calculate the CO₂ mineralization rate of our electrolyzer, i.e., r_{CaSiO_3} . We take the calculation of r_{CaSiO_3} for our weathering electrolyser purged with simulated flue gas as an example.

Given that 0.4992 g of CaCO₃ precipitated in the cathode chamber, the mass of CO₂ captured and converted into CaCO₃ in the weathering electrolyzer (m_{CO_2}) was calculated based on the following equation,

$$m_{CO_2} = \frac{m_{CaCO_3} M_{CO_2}}{N_{CaCO_3/CO_2} M_{CaCO_3}}$$
$$m_{CO_2} = \frac{0.4992 \text{ g} \times 44.01 \text{ g mol}^{-1}}{1 \times 100.09 \text{ g mol}^{-1}} = 0.2195 \text{ g}_{CO_2}$$

where N_{CaCO_3/CO_2} is the stoichiometric ratio of CaCO₃ to CO₂ (i.e., 1).

Then, the mass of dissolved CaSiO₃ during electrolysis (m_{CaSiO_3}) was calculated in the following equation.

$$m_{CaSiO_3} = \frac{it \text{ } SA \text{ } M_{CaSiO_3}}{N_{e/CaSiO_3} F}$$
$$m_{CaSiO_3} = \frac{0.1 \text{ A cm}^{-2} \times 4 \text{ cm}^2 \times 1 \text{ h} \times 116.16 \text{ g mol}^{-1}}{2 \times 96485 \text{ C mol}^{-1}} = \frac{0.4 \text{ A} \times 3600 \text{ s} \times 116.16 \text{ g mol}^{-1}}{2 \times 96485 \text{ A s mol}^{-1}}$$
$$= \frac{167270 \text{ A s g mol}^{-1}}{192970 \text{ A s mol}^{-1}} = 0.8668 \text{ g}_{CaSiO_3}$$

where $N_{e/CaSiO_3}$ is the stoichiometric ratio of electrons to CaSiO₃ in Fig. 1 (i.e., 2).

Thus, the CO₂ mineralization rate of our weathering electrolyser over 1 hour of electrolysis was calculated as follows:

$$r_{CaSiO_3} = \frac{m_{CO_2}}{m_{CaSiO_3} t}$$

$$r_{CaSiO_3} = \frac{0.2195 g_{CO_2}}{0.8668 g_{CaSiO_3} \times 1 h} = 0.2532 g_{CO_2} g_{CaSiO_3}^{-1} h^{-1}$$

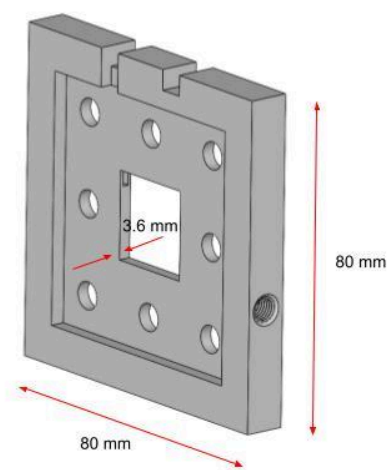
Lastly, to compare to natural weathering, we calculate the yearly CO₂ mineralization rate of our weathering electrolyzer operating at current density of 100 mA cm⁻² with simulated flue gas (10% CO₂) purging into catholyte:

$$r_{CaSiO_3} = \frac{0.2532 g_{CO_2}}{g_{CaSiO_3} h} \times \frac{24 \times 365 h}{yr}$$

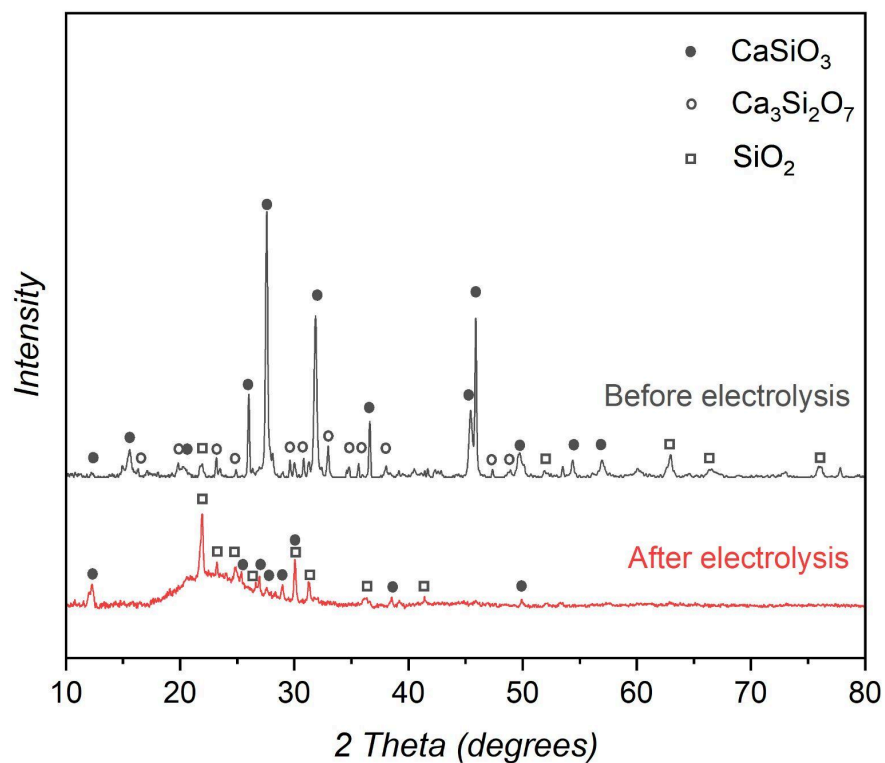
$$= 2218 g_{CO_2} g_{CaSiO_3}^{-1} yr^{-1} = 2218 ton_{CO_2} ton_{CaSiO_3}^{-1} yr^{-1}$$

Similarly, the CO₂ mineralization rate of our weathering electrolyser using CaSiO₃ and purging with ambient air is calculated to be 69.32 ton_{CO₂} ton_{CaSiO₃}⁻¹ yr⁻¹.

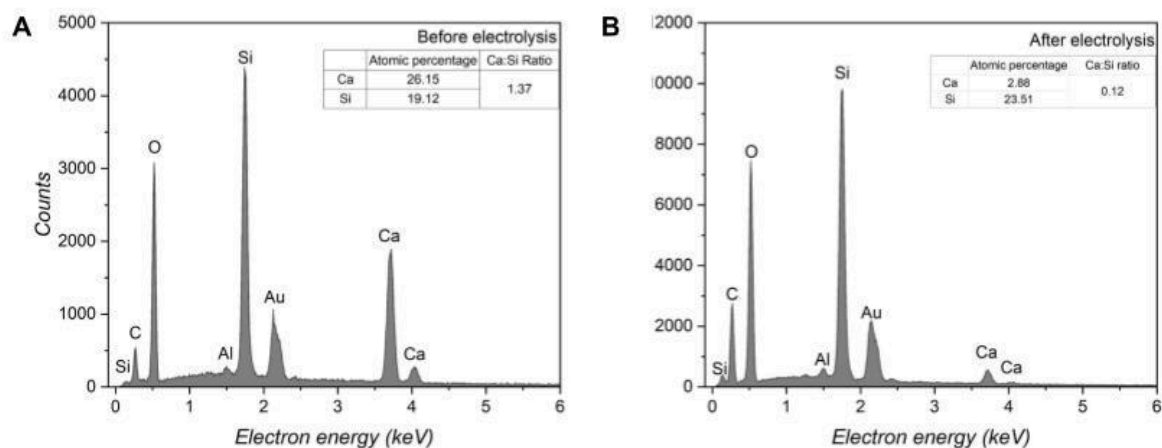
Supplementary Figures



Supplementary Figure 1: Dimensions of the 3D-printed chemical chamber.



Supplementary Figure 2: XRD diffractograms of CaSiO_3 introduced into the chemical chamber before electrolysis,^{2,3} and the solids collected in the chemical chamber after 1 hour of electrolysis. Note that the CaSiO_3 signals are less prominent after electrolysis, and the onset of the broad signal at 25 degrees is consistent with amorphous SiO_2 .⁴⁻⁶

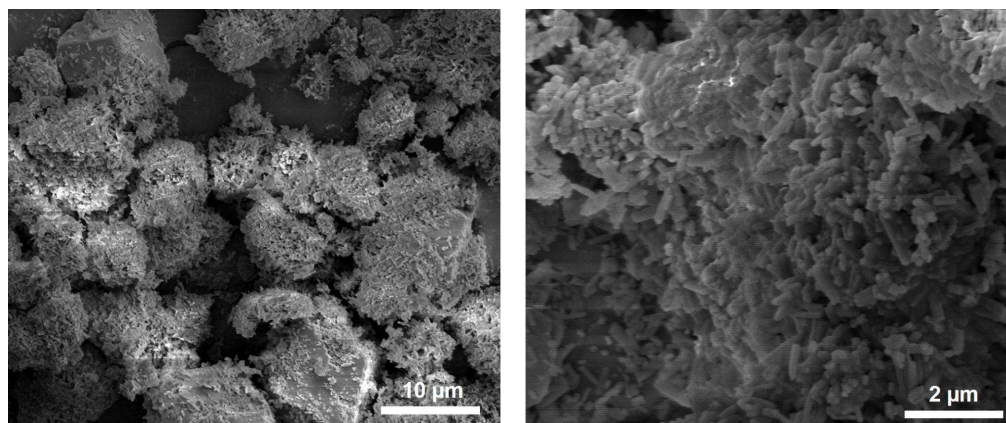


Supplementary Figure 3: EDX spectra of commercial CaSiO_3 (**A**) before and (**B**) after 60 minutes electrolysis. Gold sputtering was applied for SEM sample preparation. The detection of carbon and aluminum was assigned to conductive tape and aluminum sample stab.

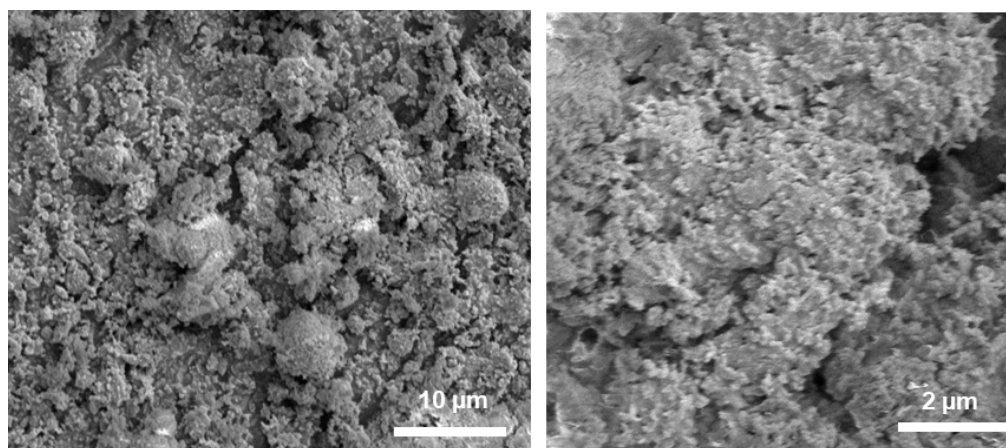


Supplementary Figure 4: Photographs of the catholyte (left) and CaCO₃ solid (right) after electrolysis at 100 mA cm⁻² in the presence of the simulated flue gas (10% CO₂, 90 % N₂) (top panel), and air (bottom panel).

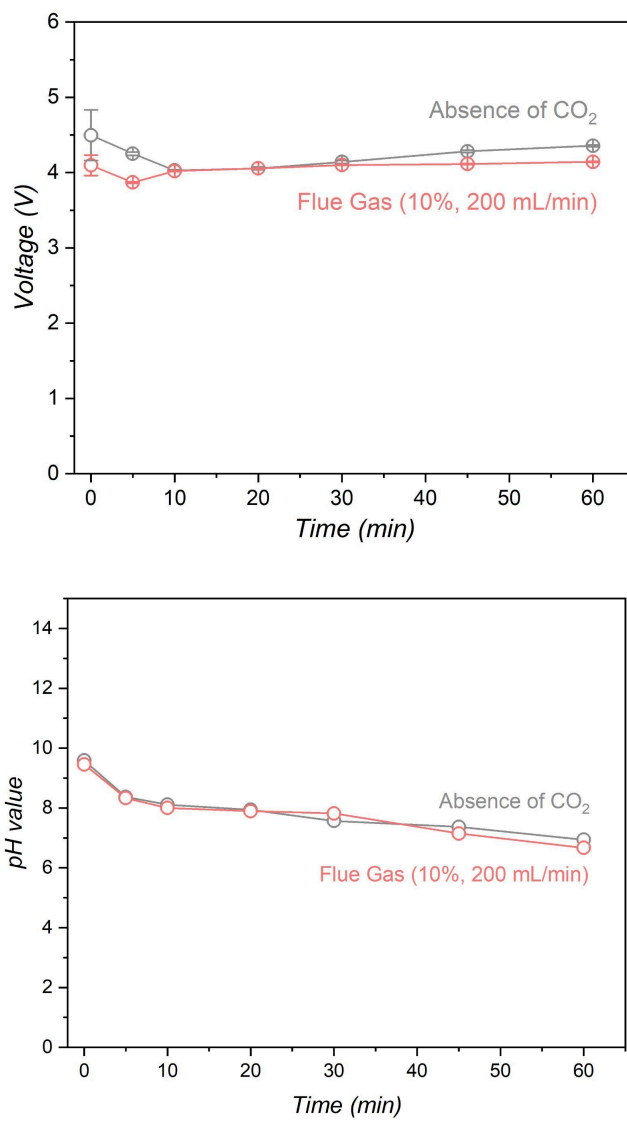
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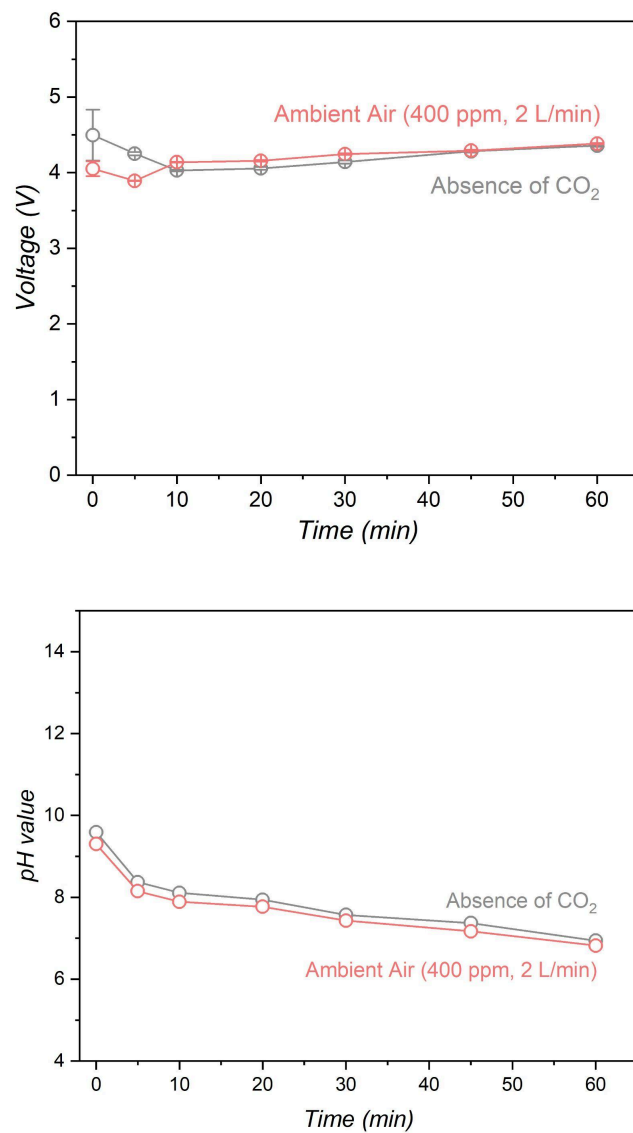
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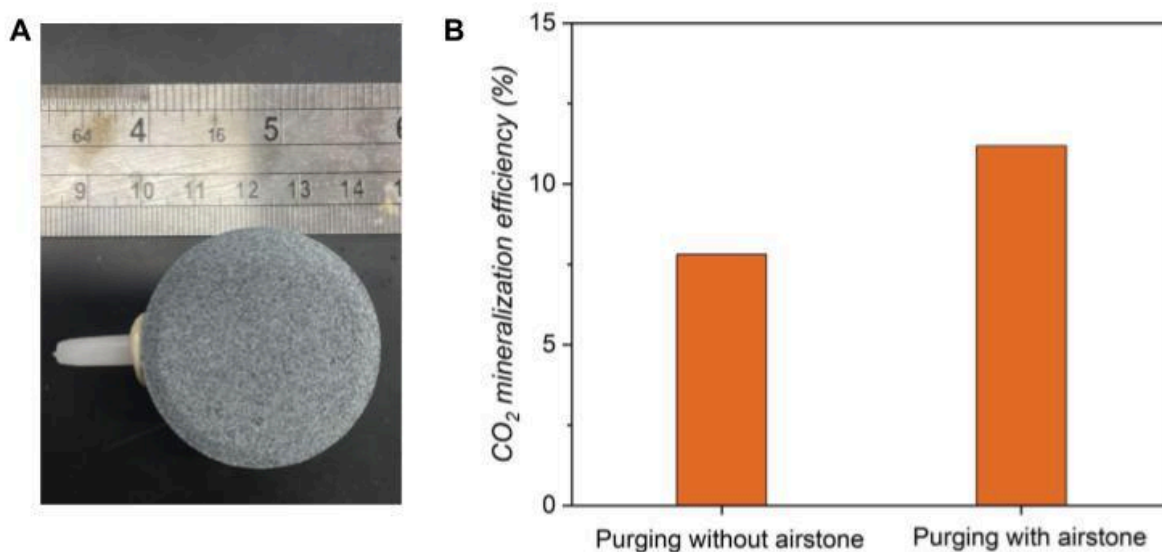
Supplementary Figure 5: SEM images of white solid recorded from the cathode chamber after electrolysis at 100 mA cm⁻² in the presence of (a) simulated flue gas (10% CO₂, 90 % N₂) and (b) ambient air.



Supplementary Figure 6: Cell voltage (top) and catholyte pH (bottom) versus time for electrolysis at 100 mA cm^{-2} without a CO_2 supply, in the presence of the simulated flue gas (10% CO_2 , 90 % N_2).



Supplementary Figure 7: Cell voltage (top) and catholyte pH (bottom) versus time for electrolysis at 100 mA cm^{-2} with and without a CO_2 supply, in the form of air.



Supplementary Figure 8: (A) The commercial airstone (diameter = 4 cm) used to purge ambient air. (B) The CO₂ mineralization efficiency of the weathering electrolyzer at 100 mA cm⁻² supplied with air, with and without the airstone.

References

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