CO_2 removal potential and self-cleaning ability of TiO_2-based cationic molecular emulsion surface treatment on concrete pavements

Rui Bai
Marina Garcia Lopez-Arias
Professor Mirian Velay-Lizancos

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VELAY Research group

PURDUE UNIVERSITY | Lyles School of Civil Engineering

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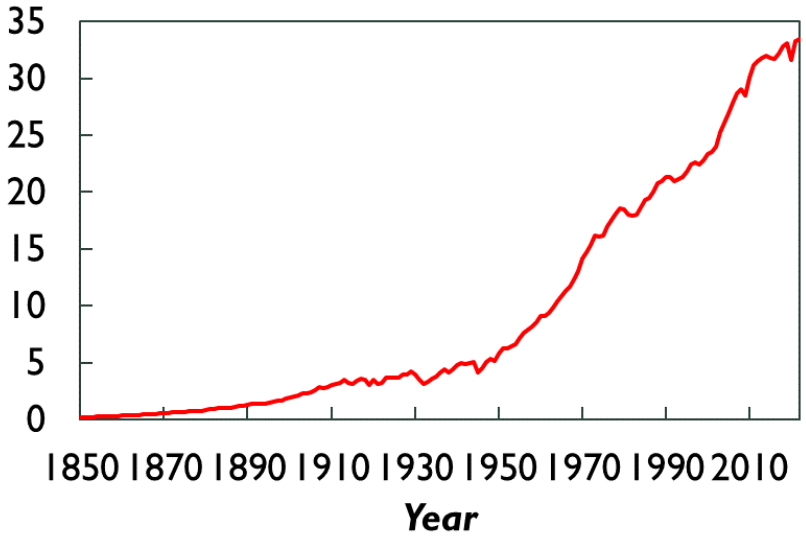
aci CONCRETE CONVENTION

Outline

1. Introduction
2. Materials
3. Methods
4. CO_2 Removal
5. Self-cleaning
6. Conclusions




Cement | Aggregates | Water



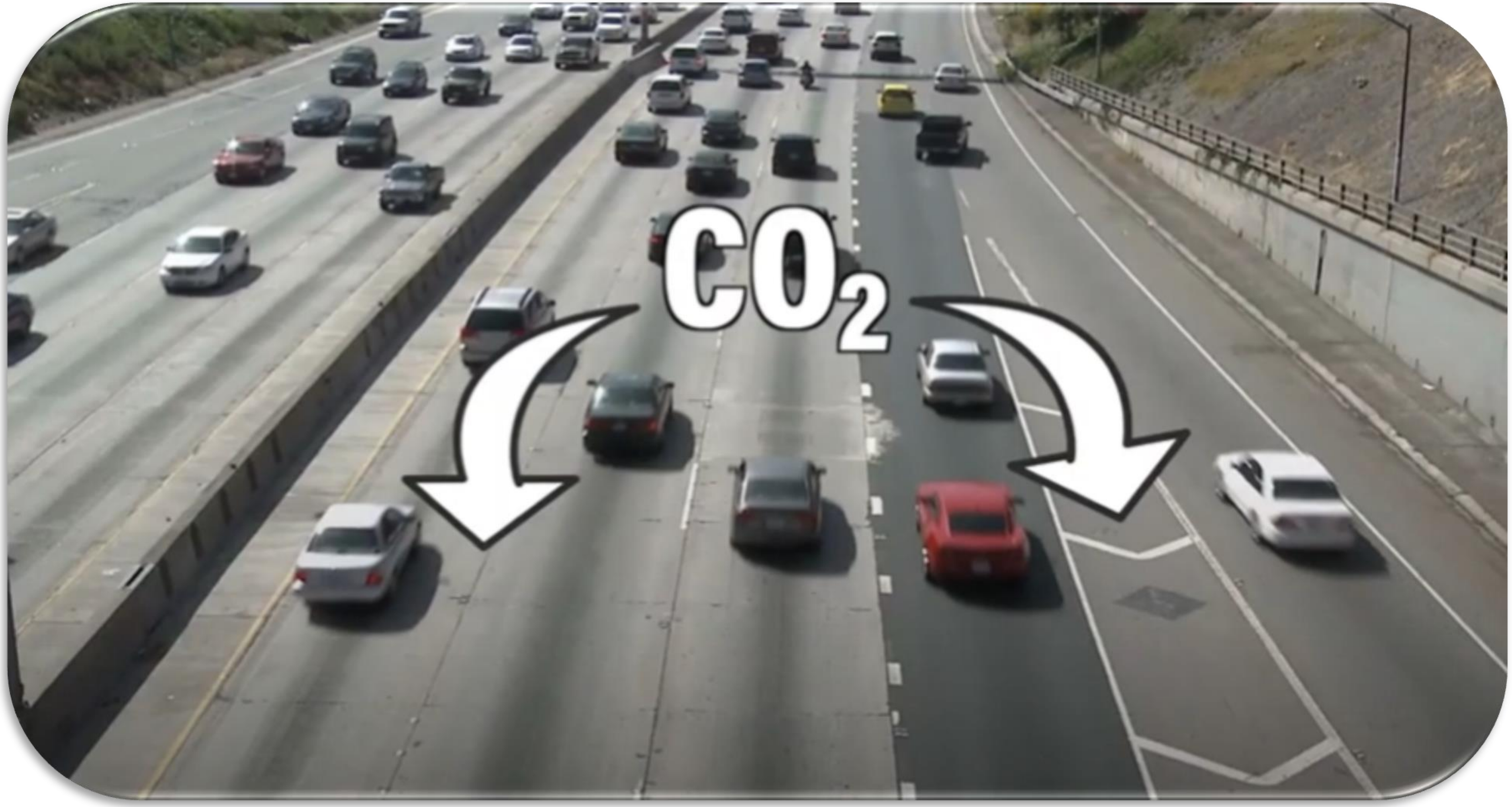
CO_2 emissions [1]

8% of the total

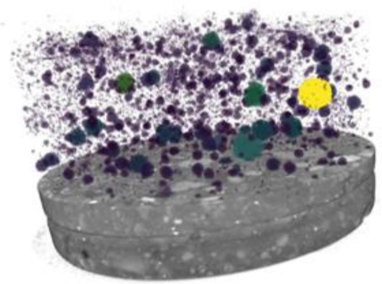
CO_2 emissions each year for cement [2]

[1] Our World in Data. https://ourworldindata.org/emissions-by-fuel
[2] Cheng et al. (2023), Nat. Commun.

Proactive sustainable properties



Carbonation: *CO_2 sequestration* in cement-based materials



Slow process

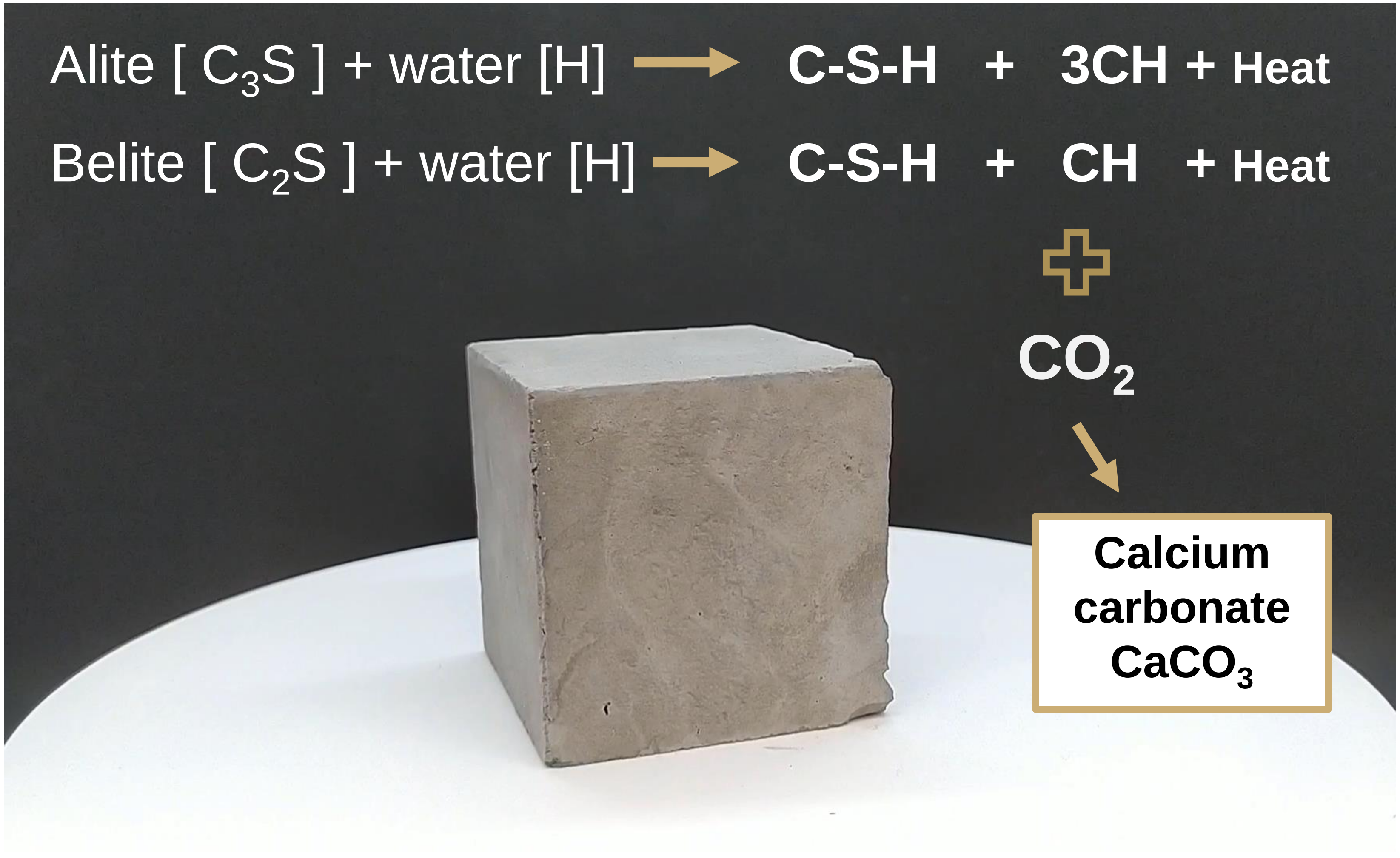
It was estimated that

↓

40% of CO_2
has been reabsorbed

Alite [C_3S] + water [H] → **C-S-H + 3CH + Heat**

Belite [C_2S] + water [H] → **C-S-H + CH + Heat**



Adding nano-TiO_2 to increase CO_2 uptake or sequestration [3]

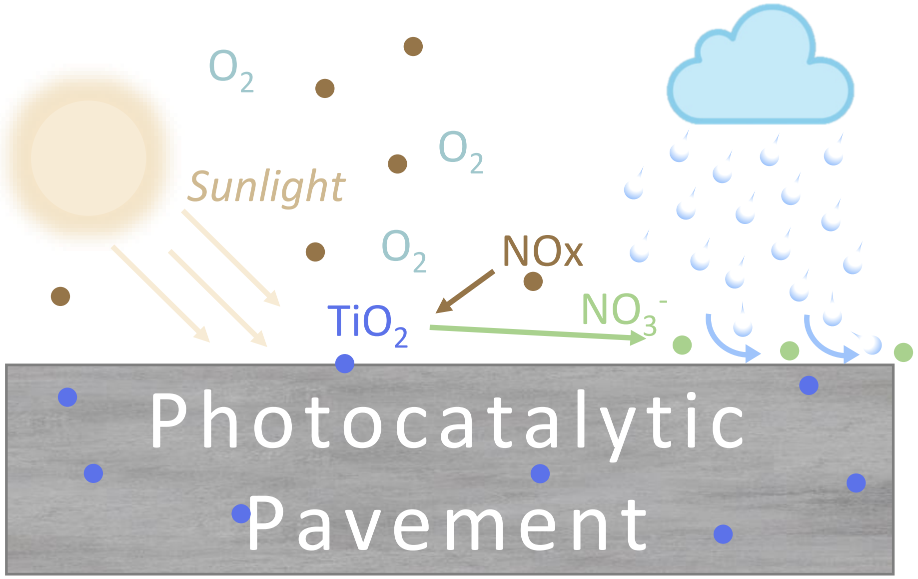
- Increases CO_2 uptake
- Enhances mechanical properties
- Provides photocatalytic properties
- Increases durability

- With the right proportions, a very small addition of nano-TiO_2 can **double the amount of naturally captured CO_2** by cementitious materials in a given period [4]
- With **lower CO_2 concentrations**, the **effectiveness** of nano-TiO_2 addition in terms of CO_2 reduction is **higher** than with 100% CO_2 [5]

What can we do for existing pavements?

[3] Bertos et al. (2004) *J. Hazard Mater*.
[4] Moro et al. (2021) *Constr. Build. Mater*.
[5] Lopez-Arias et al. (2023) *Constr. Build. Mater*.

TiO_2 surface treatment → Studied for asphalt and concrete pavements [6,7] (*NOx degradation*)

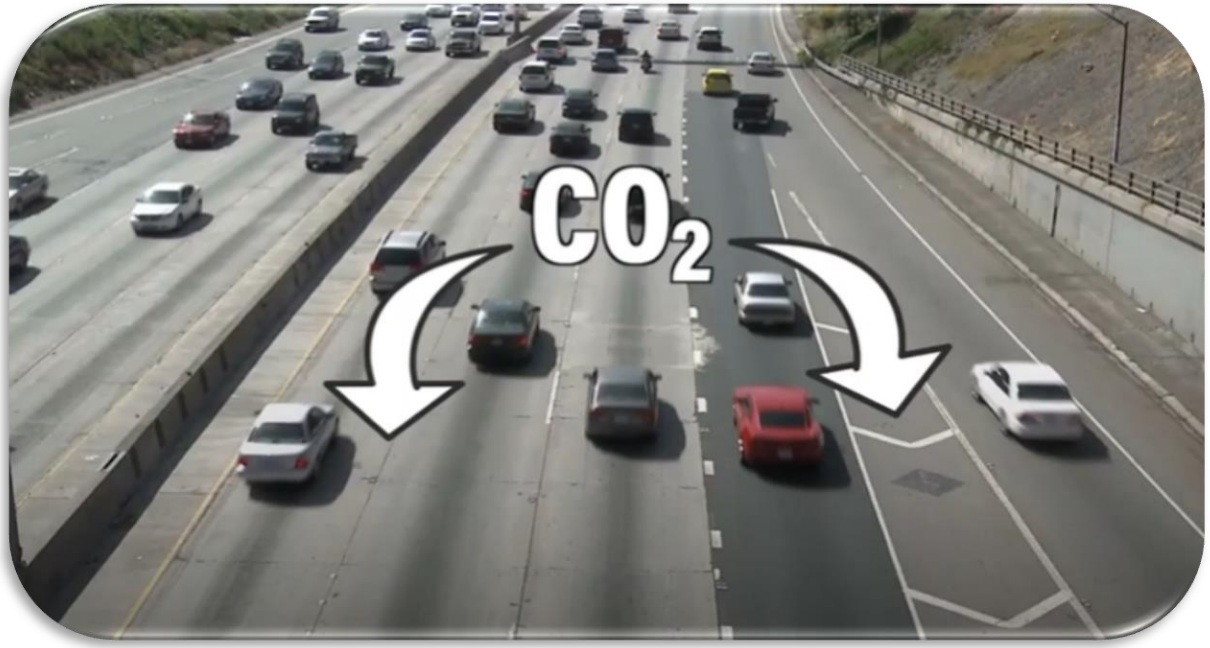


What about CO_2?

[6] Mendoza et al. (2015) *Appl. Catal. B*
[7] Yu et al. (2020) *Nanomater*.

Objective

Assess the potential use of a TiO_2-based surface treatment to turn a ***concrete pavement into a CO_2 removal agent*** in an economically and technically feasible way.



18 concrete slabs

- ✓ w/c = 0.45
- ✓ Max aggregate size = 19 mm
- ✓ Slump = 2 ¼ inches
- ✓ Air content = 6%

Slab geometry

7.85” x 3.92” x 1.57”
20 cm x 10 cm x 4 cm

- ✓ ASTM C192
- ✓ 500 division of INDOT specification for concrete pavements

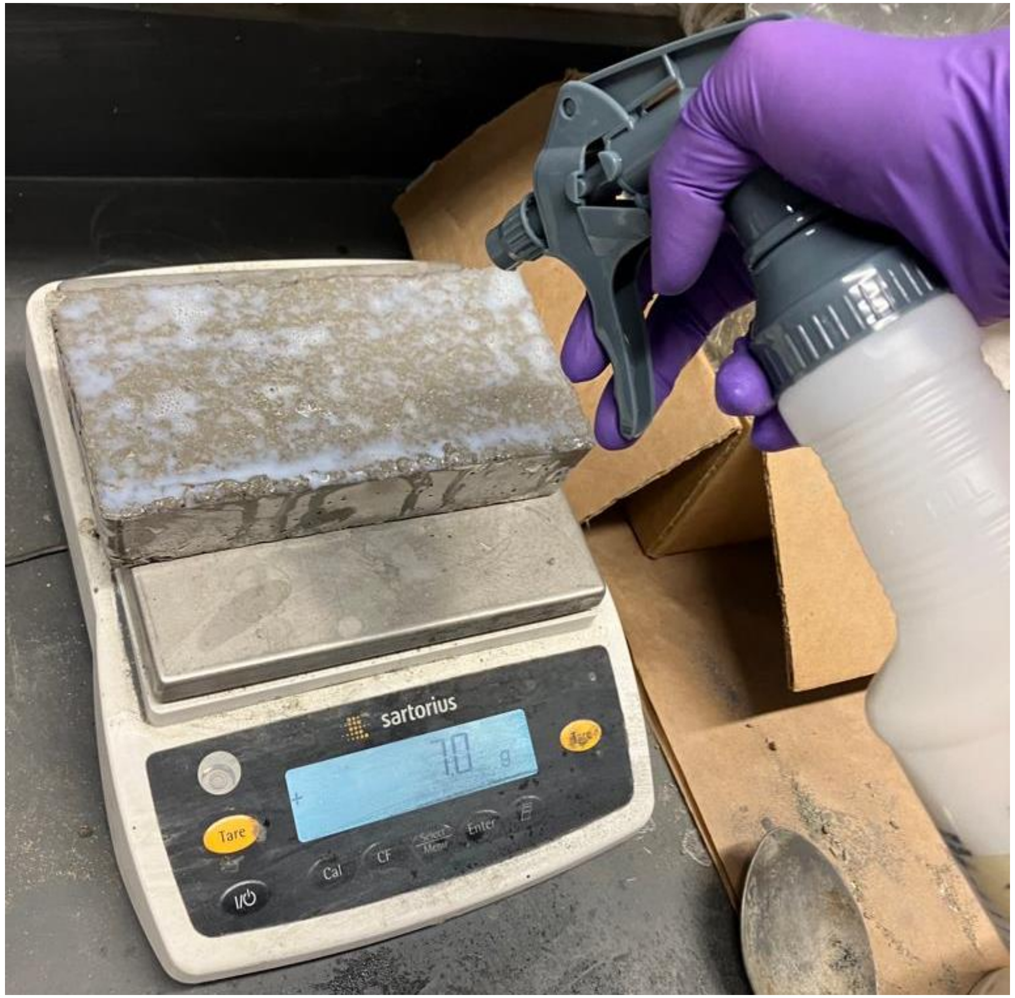
Cured for 28 days at
95 ± 5 % RH and 25 ± 1 °C

TiO_2 surface treatment

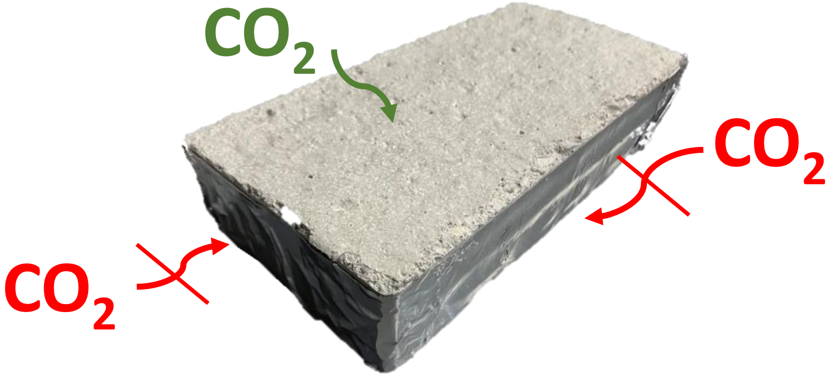
Application rate range = **0.05 - 0.08 gal/yd²**

Apply product to specimen

- Evenly sprayed on the surface until the sample increases in weight to the two application rates considered.
- Sprayed at constant distance (8''), wiping all surfaces between each pulverization

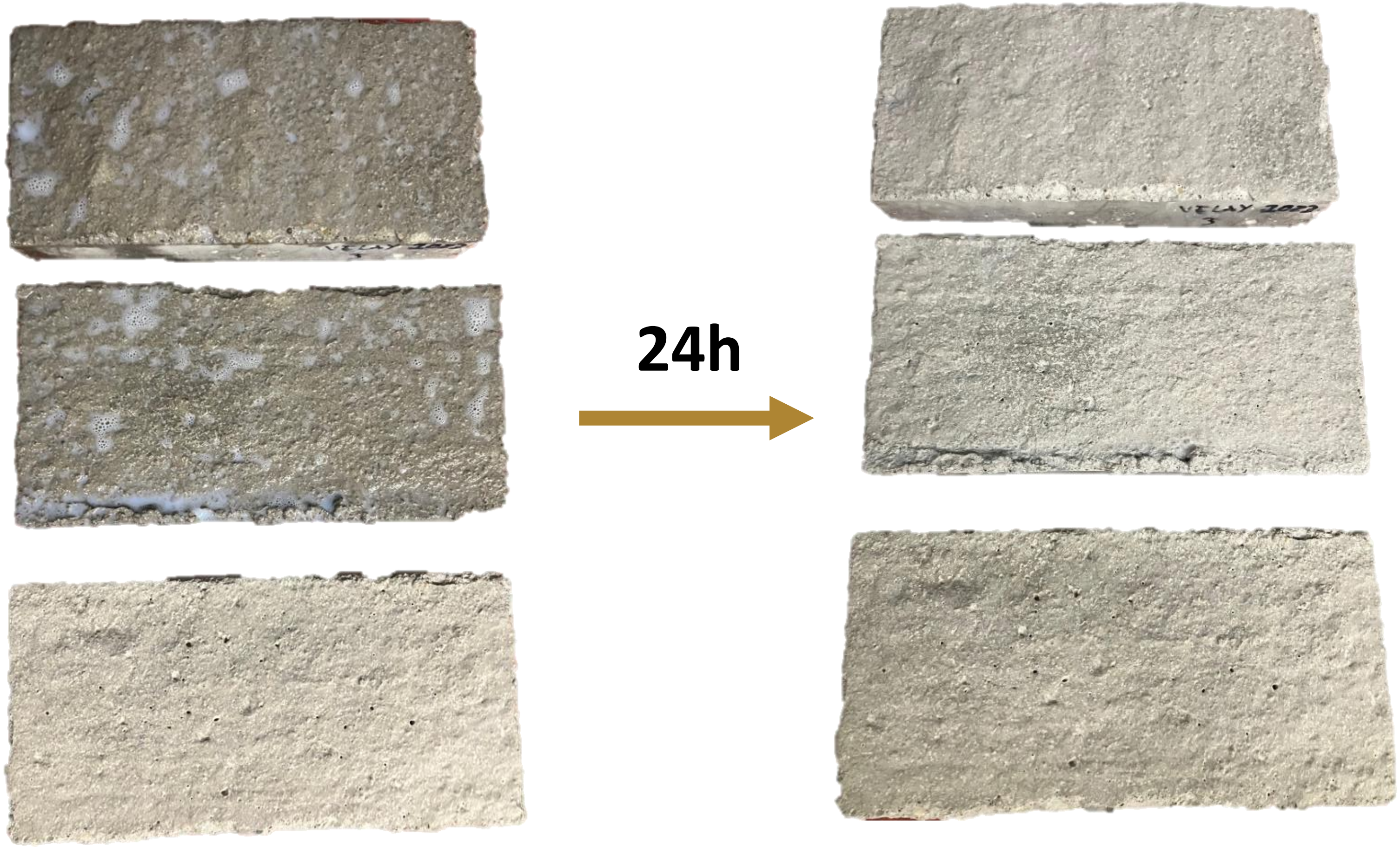


Cover other surfaces where possible carbonation can occur

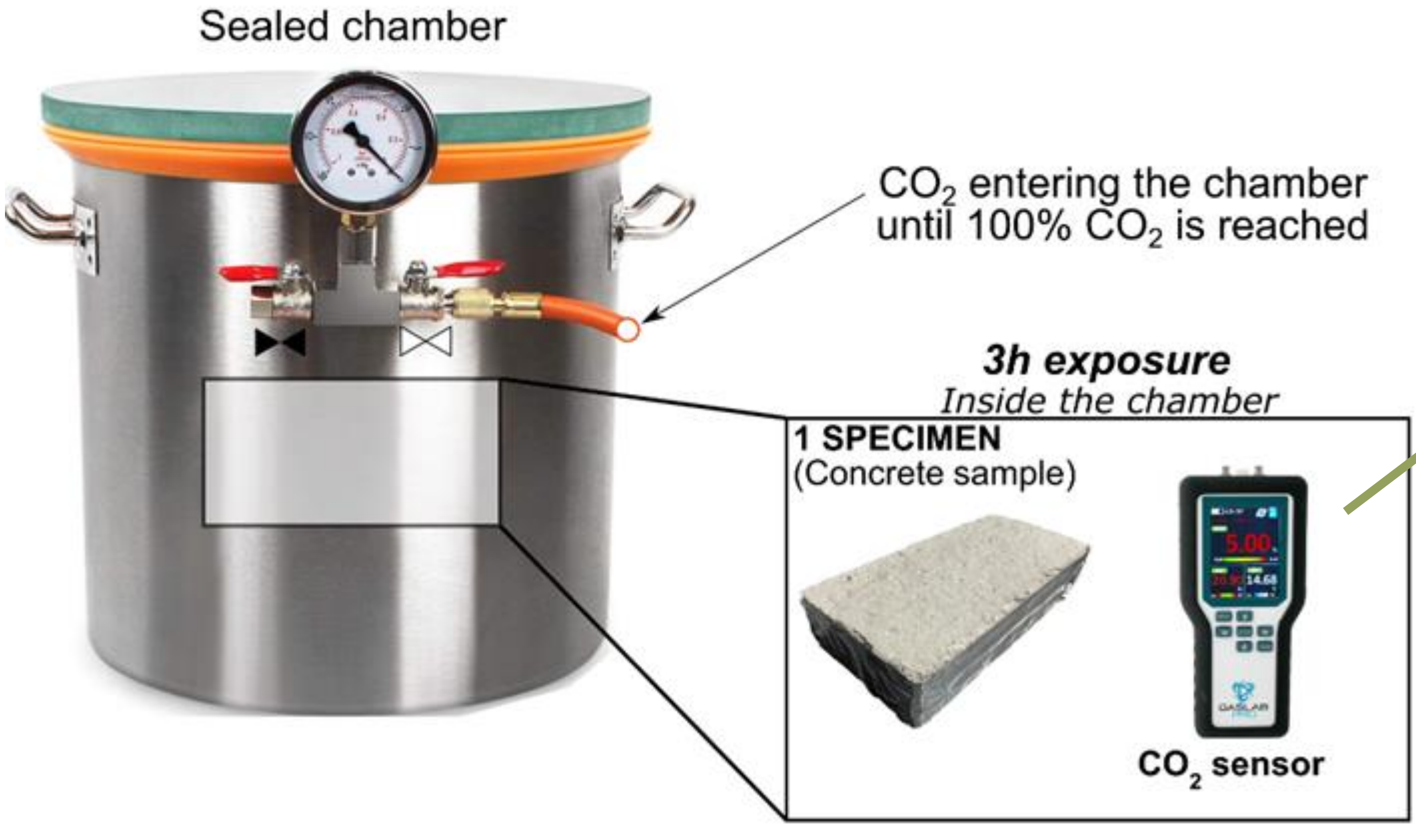


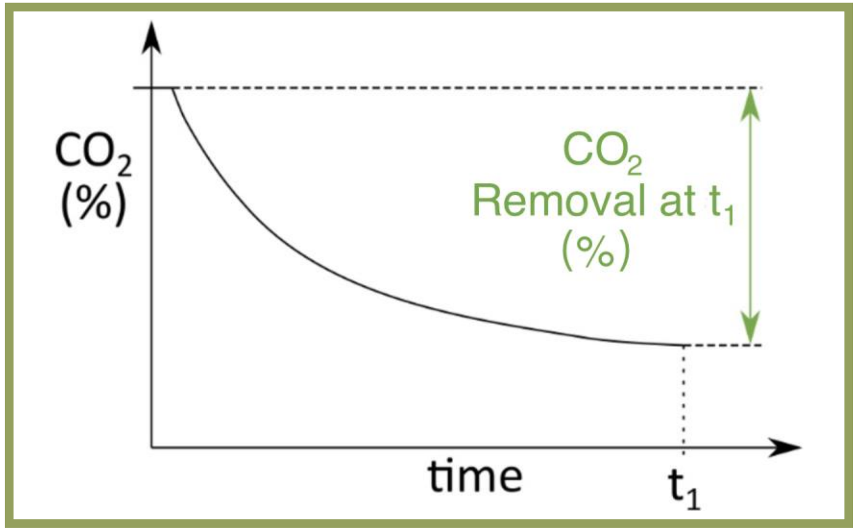
TiO_2 surface treatment

Wait for the product to dry (24h)



CO_2 exposure

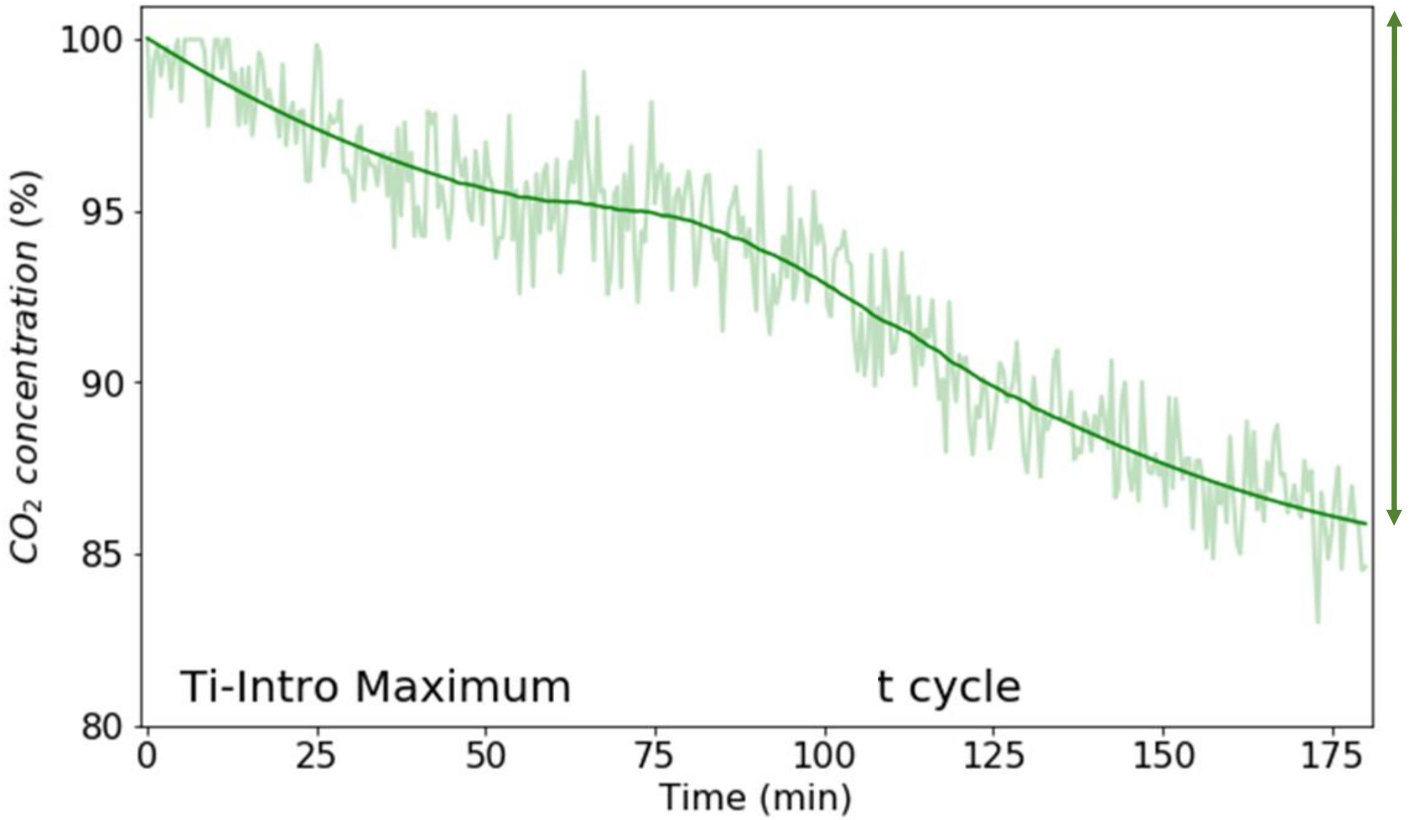




- ➢ Two CO_2 exposure cycles of 3 hours each (a total of 6 hours of exposure)
- ➢ Sensor recording the loss of CO_2 in the chamber due to the sample's CO_2 reduction.

CO_2 reduction

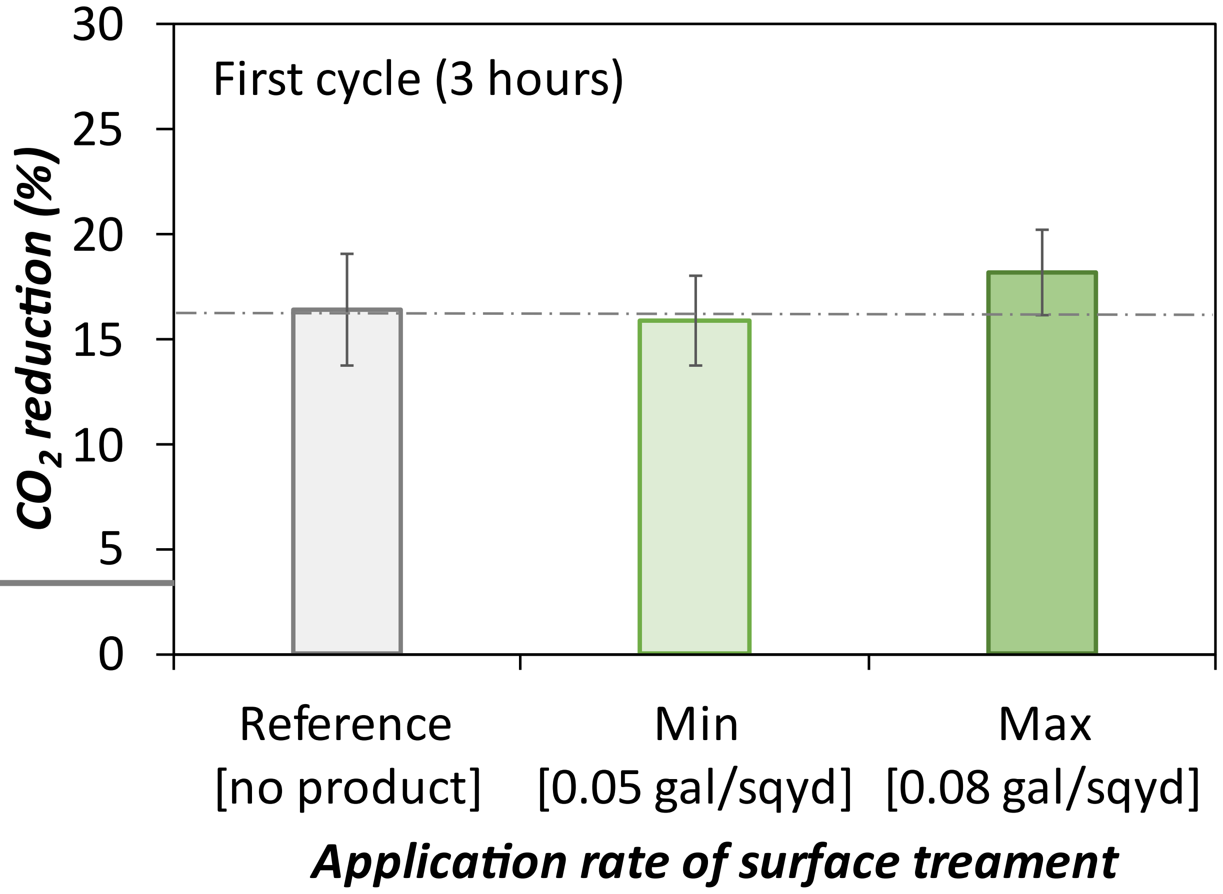
- Raw data from the CO_2 sensor: CO_2 concentration over time (3 hours)
- 3 samples per condition



CO_2 reduction

$$CO_2 \text{ reduction } (\%) = \frac{\sum_{i=1}^{3}\left(\%CO_{2,start,i} - \%CO_{2,end,i}\right)}{3}$$

CO_2 Reduction Results: first 3 hours

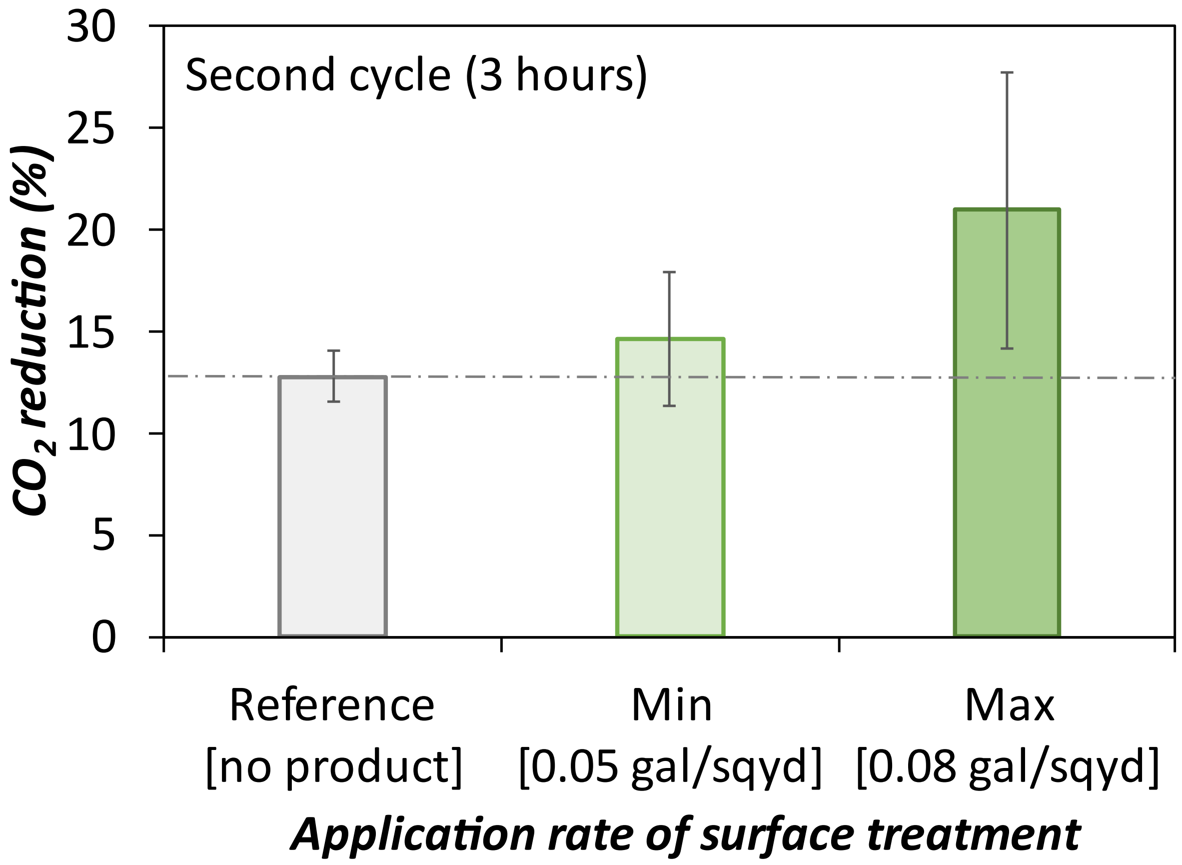


Natural carbonation

Limited, it will go to zero over time because the accessible hydration products will be consumed at some point.

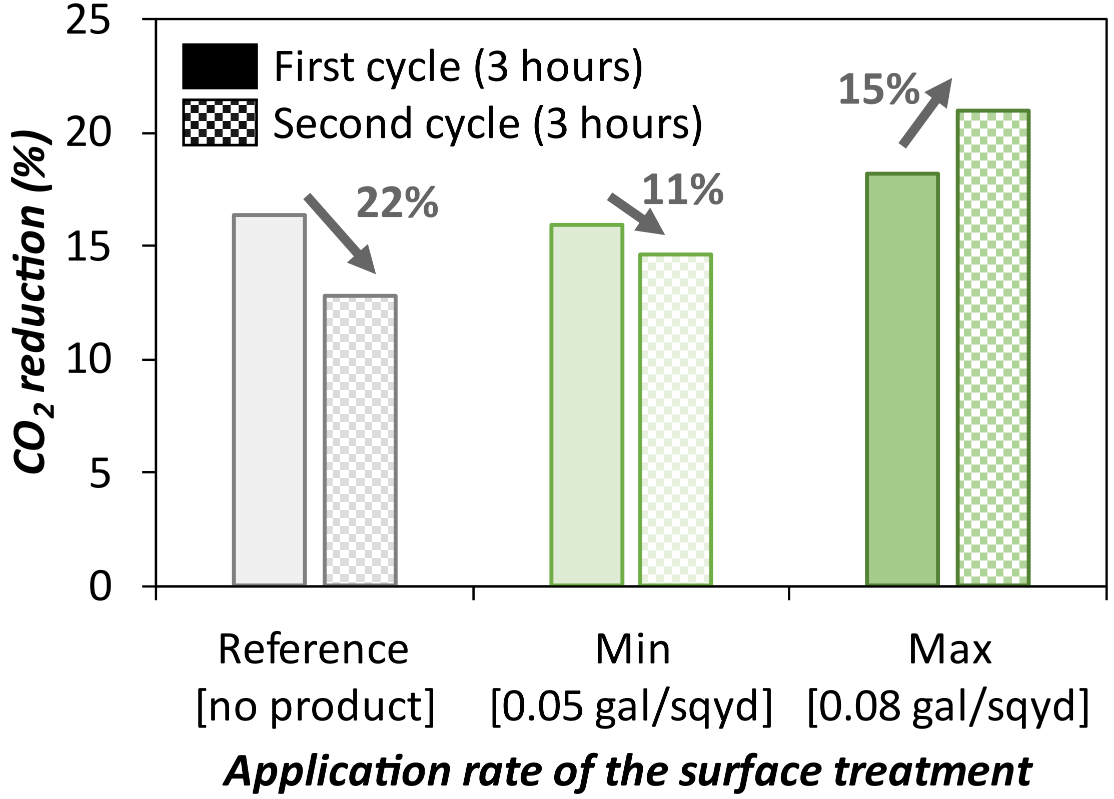
CO_2 reduction can be mainly attributed to **carbonation** in both treated and untreated samples

CO_2 Reduction Results: next 3 hours



In the **second cycle**, the use of the maximum application **rate surface treatment made a significant increase on the CO_2 reduction** compared to the reference group

CO_2 Reduction Results



Reference:
Carbonation slowing down over time

Minimum app rate:
Less pronounced

Maximum app rate:
Trend **reversed**

The TiO_2 surface treatment enhances CO_2 reduction

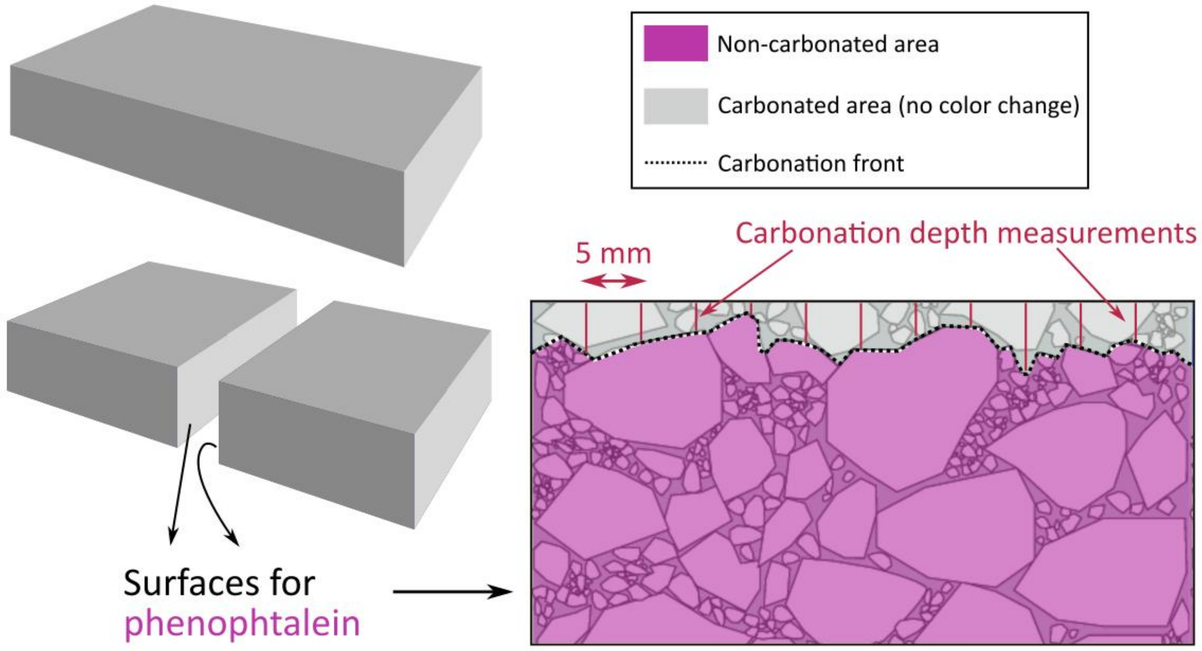
Phenolphthalein test ←

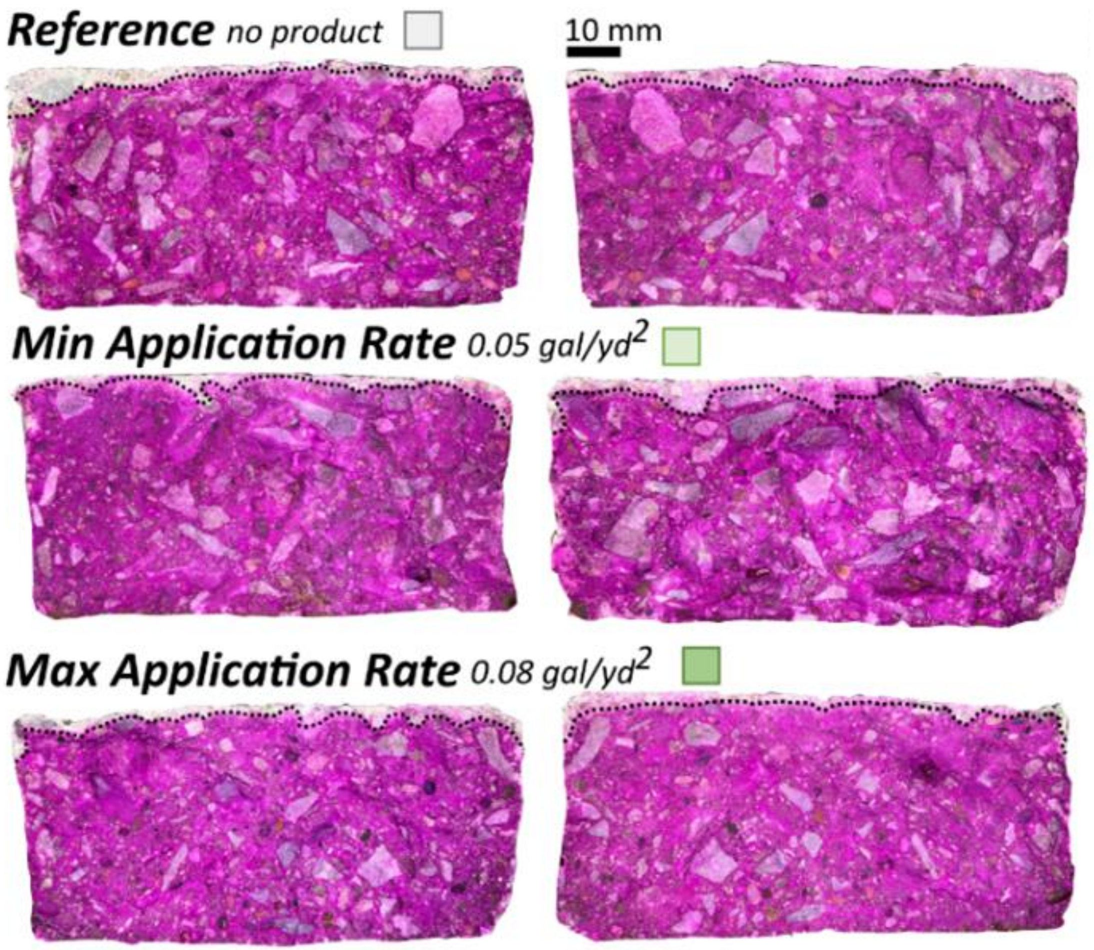
Two possible explanations:

(i) Enhancement of **carbonation**

(ii) Reduction of CO_2 through a **different mechanism**

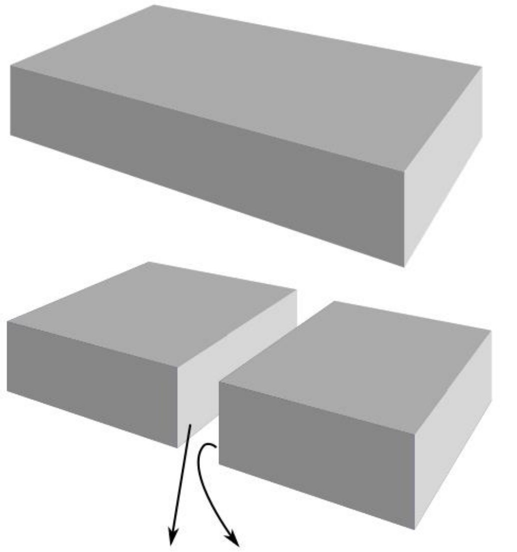
Phenolphthalein test: carbonation depth

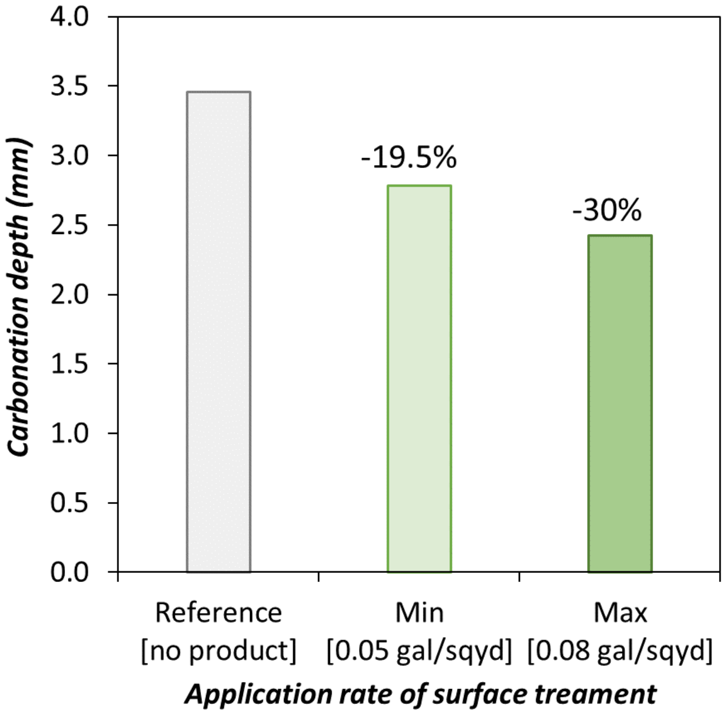


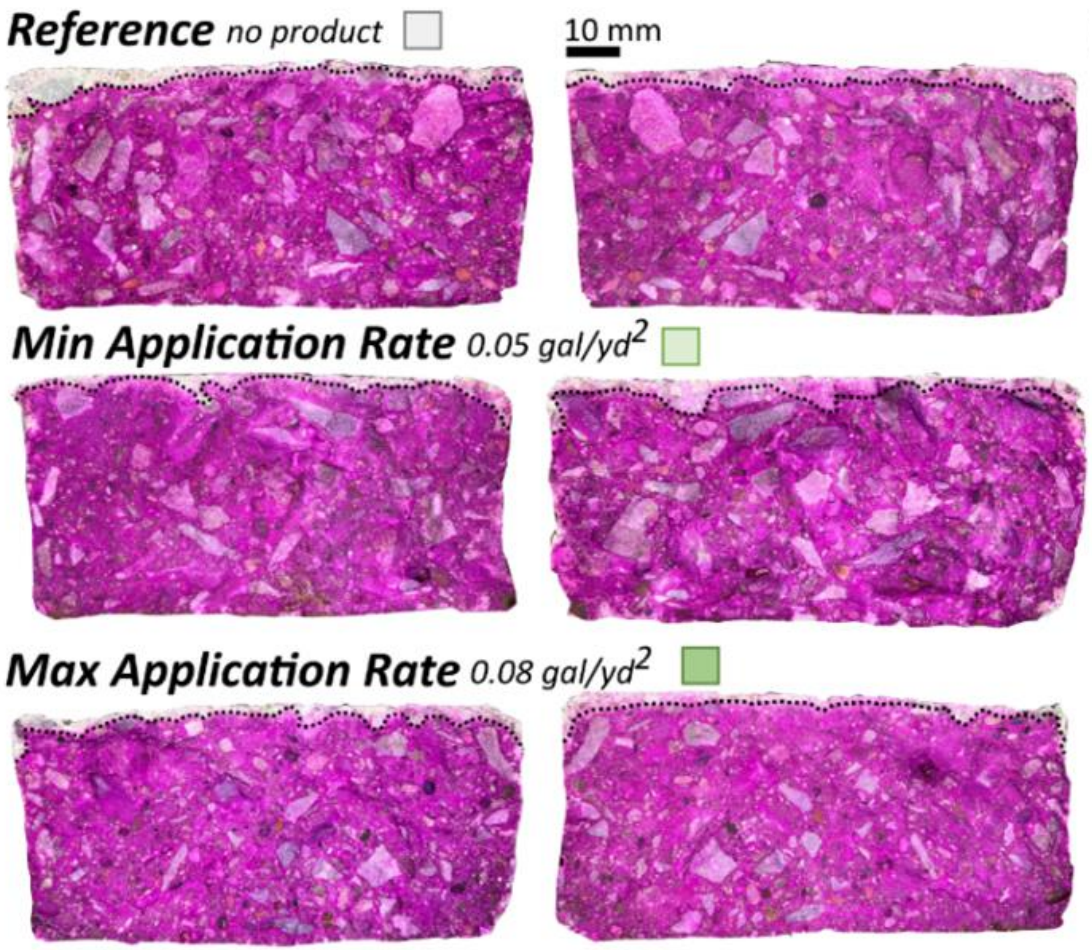


- **Carbonation depth is not affected** by the **surface** treatment.

Phenolphthalein test: carbonation depth







- **Carbonation depth is not affected** by the **surface** treatment.
  - It even decreases in average
- Excess of CO_2 reduction with the surface treatment means that a **CO_2 decomposition** might be happening in the treated samples.

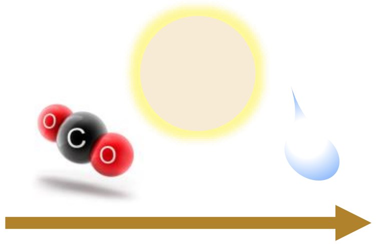
→

- May not be limited
- No corrosion concern

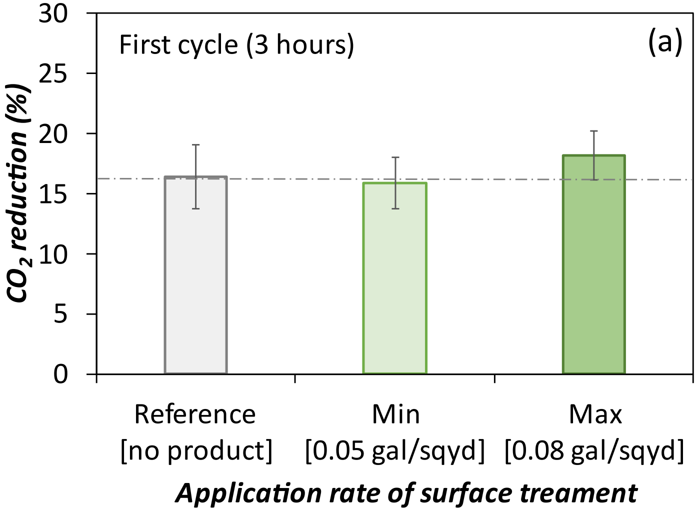
[8] Ola et al. (2015) *J. Photochem. Photobiol*
[9] Li et al. (2014) *Catal. Today*
[10] Moustakas et al. (2018) *Chem. Eur. J.*

CO_2 Photoreduction

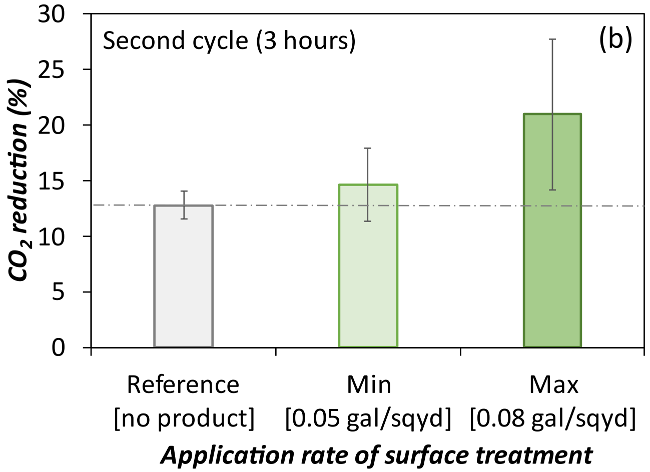
- Reducing CO_2 through photocatalysis has been studied for TiO_2 alone [8,9]



Oxygen (O_2)
Carbon monoxide (CO)
Hydrogen (H_2)
Methanol (CH_3OH)
[10]



Carbonation and photoreduction compete in first cycle



With carbonation slowing down, it is suggested that photoreduction overshadows carbonation

- Previous carbonation might also be **positively** influencing this phenomenon

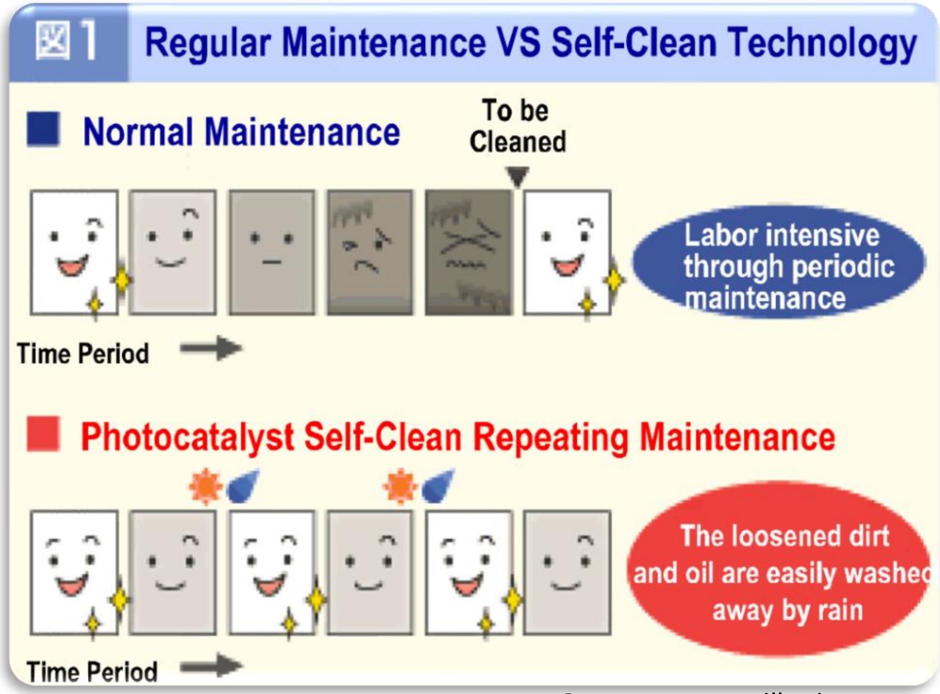
  CO_2 is directly in contact with the TiO_2 catalyst, letting it decompose before penetrating

Porosity is reduced in the surface layer with carbonation

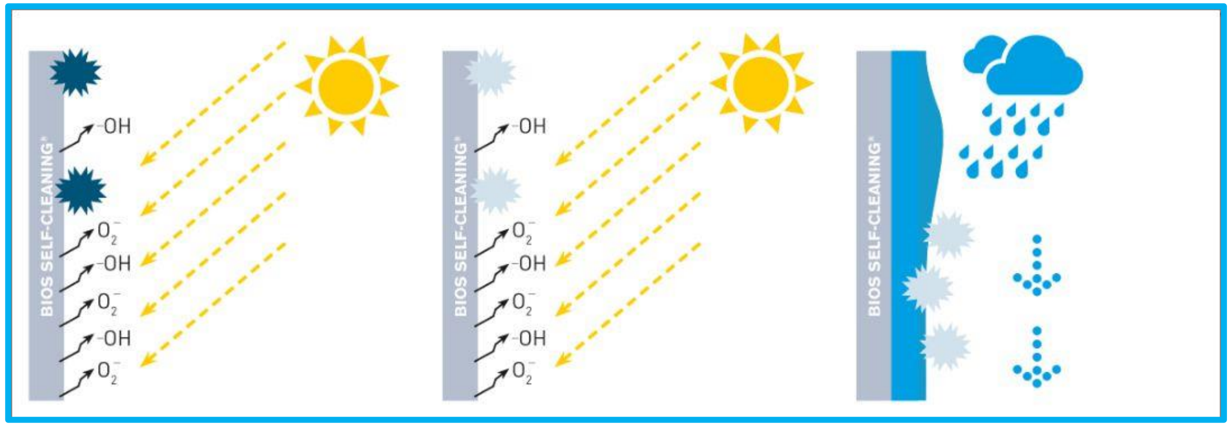
Self-cleaning Assessment

- Self-cleaning is defined as the ability to **eliminate pollutants** from the material **without the use of work**
- Self-cleaning is part of the **photocatalytic effect**, which also encompasses depollution
- Standard to determine if a material is photocatalytic:

UNI 11259: Determination Of The Photocatalytic Activity Of Hydraulic Binders Rhodamine Test Method



Source: greenmillenium.com



Source: casalgrandepadana

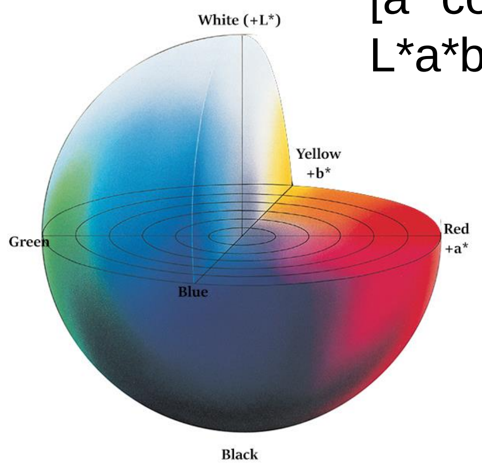
Self-cleaning Assessment

Method steps:

1. Slabs are sprayed with a dye: Rhodamine B, and set to dry for 24h in a **dark environment.**
2. Start **UV light** exposure
3. Measure color variation after 4 and 24h of UV light exposure

UNI 11259. A material is photocatalytic if:

- $\Delta a^* > 20\%$ at 4 hours of UV light
- $\Delta a^* > 50\%$ at 24 hours of UV light

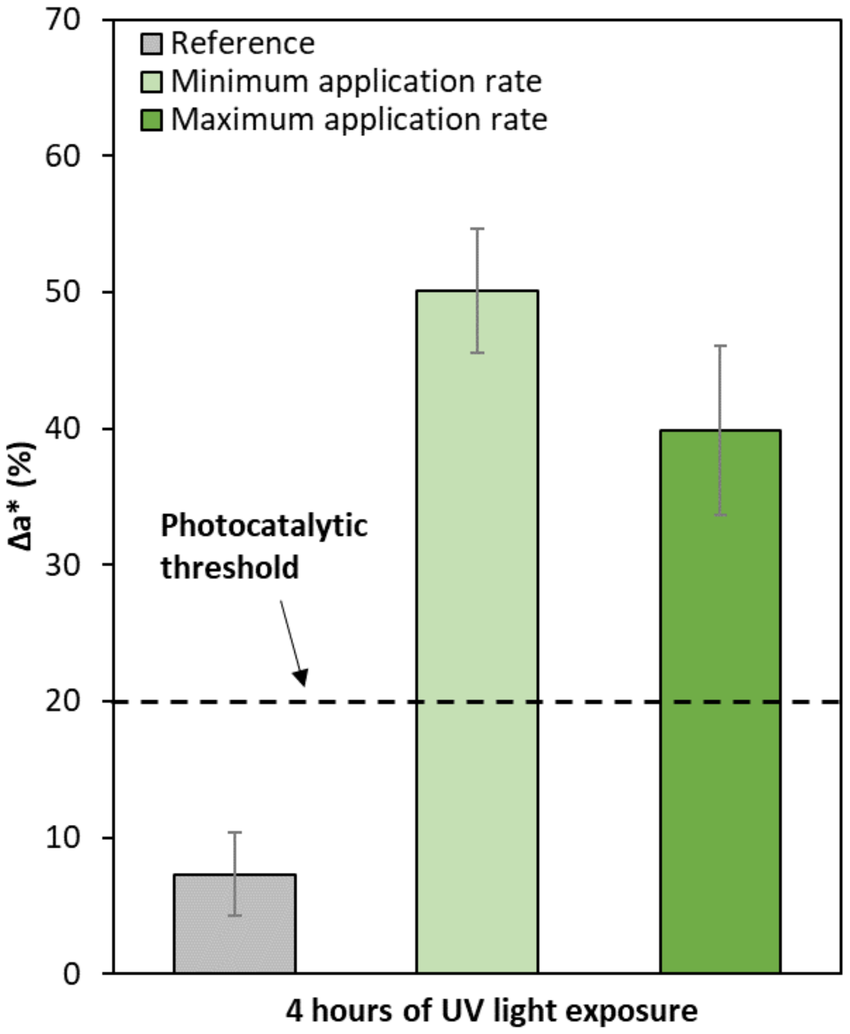


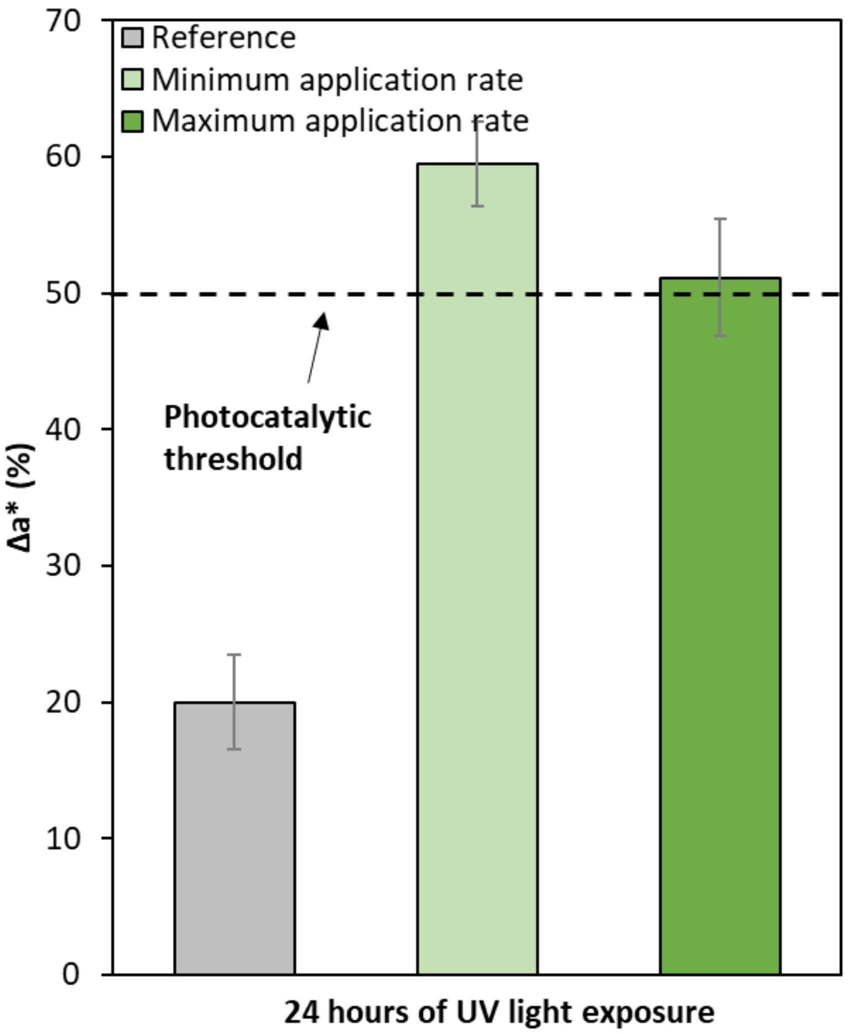
[a* coordinate: green to red axis in the L*a*b* color spectrum]

$$\Delta a^* = a_t^* - a_0^*$$

Spectrophotometer: equipment to measure color

Self-cleaning Assessment : Results

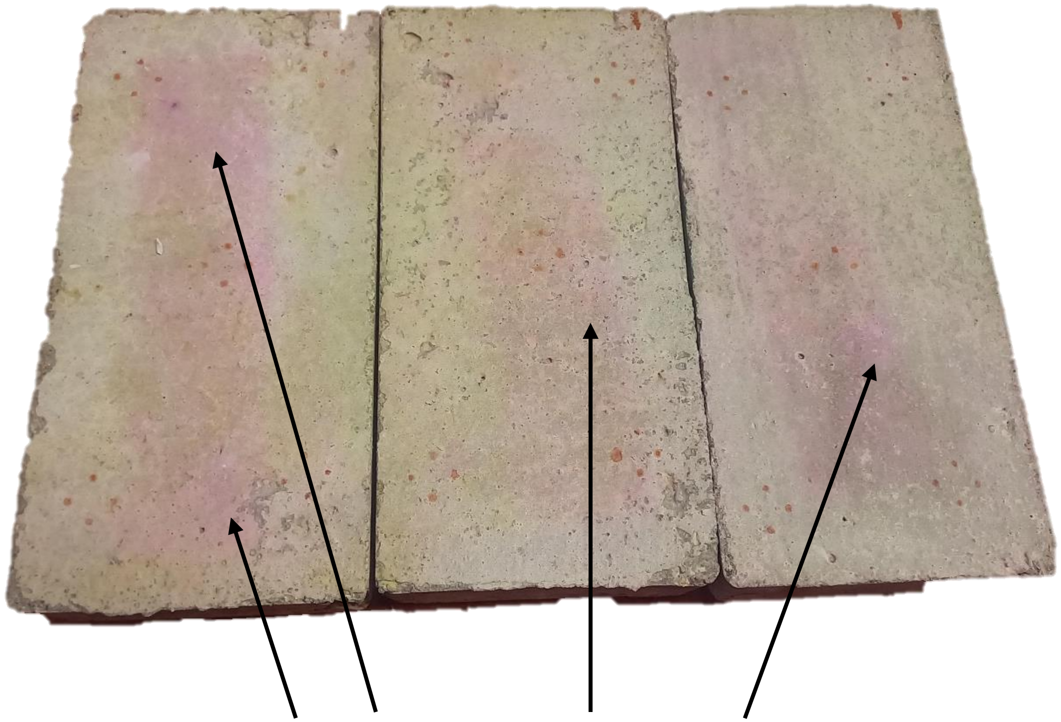




- ✓ Both application rates **are above the standard's threshold** for a photocatalytic material
- ✓ The test was performed on the ***rough surface*** of the material producing some variation on the results.

Self-cleaning Assessment : Visual evaluation

Samples without product



Pink dye still visible in all specimens

Samples with the surface treatment applied

The dye completely disappeared in all samples

Final Remarks

- The TiO_2-based surface treatment **enhanced the concrete's CO_2 reduction ability**.
- As the phenolphthalein test confirmed, the increase in the CO_2 reduction produced by the treatment is **not related to an increase in carbonation** depth. Thus, results suggest **photocatalytic conversion of CO_2.**
- The surface **carbonation** at the beginning of the CO_2 exposure **competes** with the potential **photoreduction** ability that the treatment for the available CO_2. This makes the treatment's effect on the CO_2 reduction during the first exposure negligible. However, **treated samples showed a greater CO_2 reduction in the second cycle** than reference samples.
- Carbonation during the first hours might **enhance the effectiveness of the treatment in terms of CO_2 reduction in the next hours**. The **reduction of surface porosity** due to carbonation slows down the penetration of CO_2 and leaves **more CO_2 on the surface to react** with the TiO_2.
- The self-cleaning test shows that the treated sample all **meets the threshold** of photocatalytic material.
- Part of these results have been ***submitted for publication***. Currently: under review.

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Thank you for your attention!

Rui Bai [presenter]
Marina Garcia Lopez-Arias
Professor Mirian Velay-Lizancos

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