Accelerating CO_2 Uptake in Cement Pastes through Nano-TiO_2 Modification

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aci CONCRETE CONVENTION

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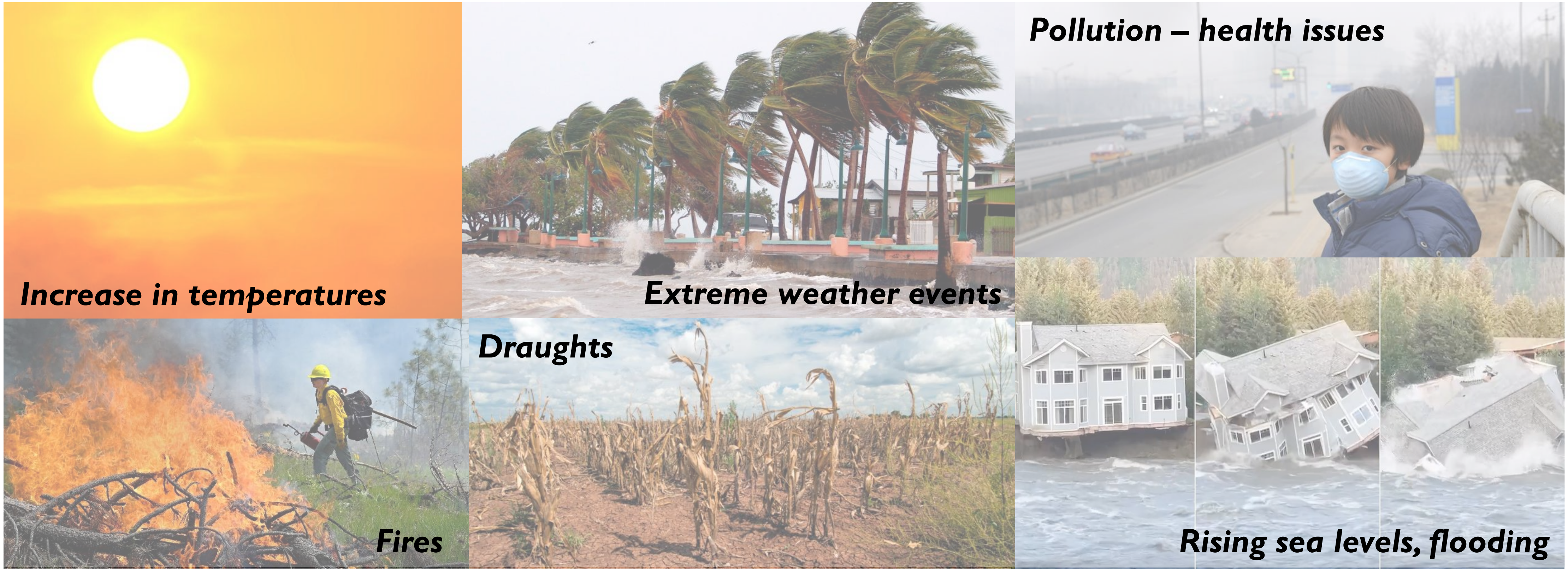
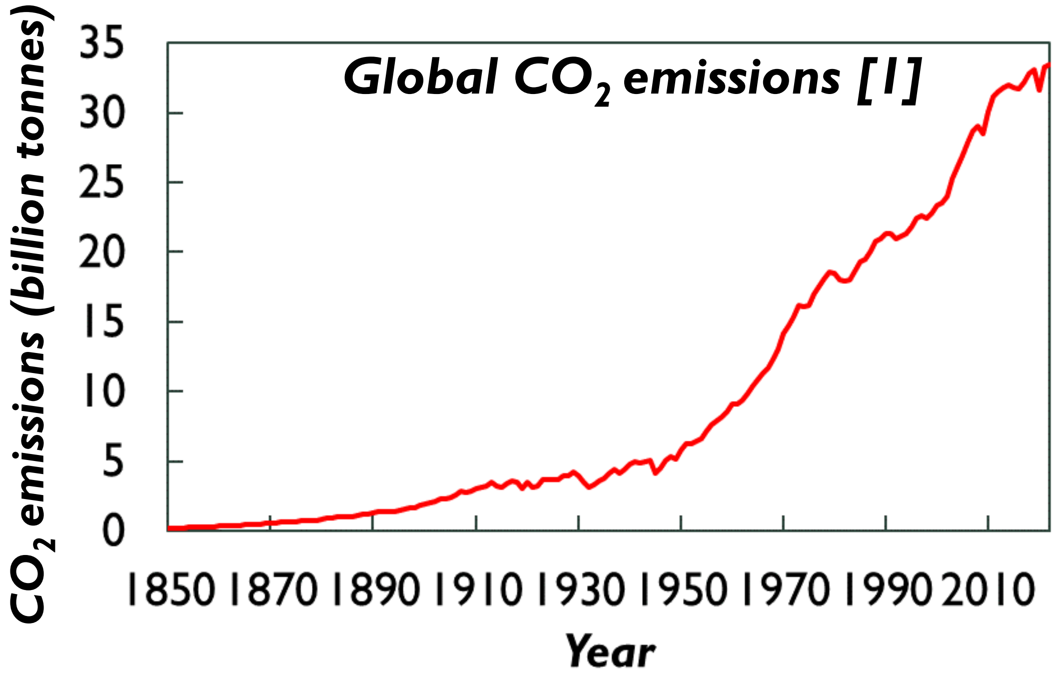
Climate change



Climate change



Alarming CO_2 rising levels

WHO IS RESPONSIBLE?

Influence of the **construction and buildings sector**

CONCRETE

most used construction material in the world




Cement | Aggregates | Water

8% of the total
CO_2 emissions each year [2]

Due to the broad and wide use of

CONCRETE

↓

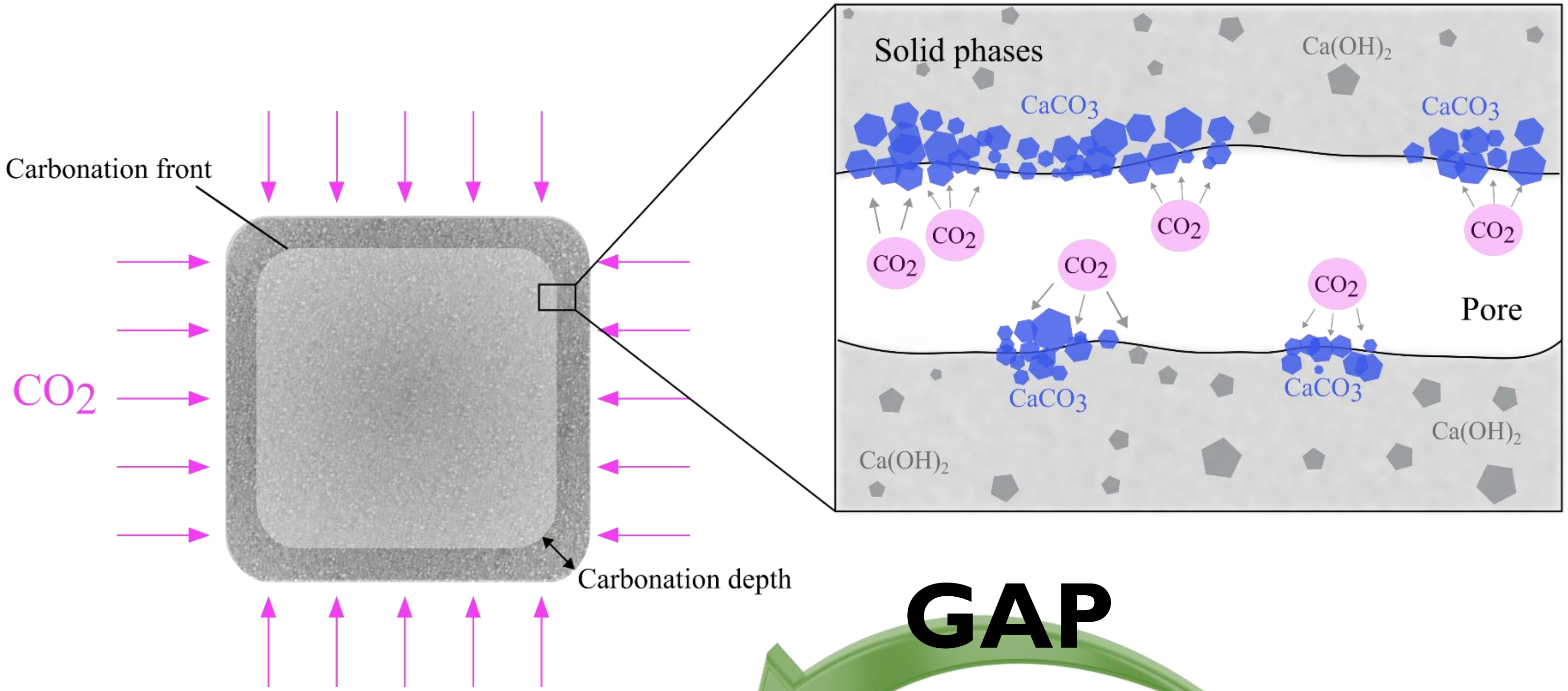
OPPORTUNITY

↓

CONCRETE

PART OF THE ***SOLUTION***

Carbonation: CO_2 *sequestration* in cement-based materials



$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$ [3]

Slow and long process

Ways to accelerate it [4]

CO_2 curing

- Increases CO_2 uptake [5]
- Increases compressive strength [6]

Adding nano-TiO_2

- Enhances mechanical properties [8]
- Provides photocatalytic properties [9]
- Increases durability [10]

Our previous study:

- **Increases CO_2 uptake [7]**

GAP

The effect of **nano-TiO_2** and **CO_2 concentration** on the **CO_2 uptake rate is not yet known**

Objective

To understand the fundamental mechanisms that govern the **CO_2 uptake rate variations** produced by ***nanomodification*** of cement pastes and ***CO_2 concentrations.***

2. Materials & Methods

OPC:Type I

Water

Nano-TiO_2

0% and 1%

Cement pastes

16x4x4 cm^3

w/c **=** 0.55

CP0

0% nano-TiO_2

CP1

1% nano-TiO_2

Curing procedure

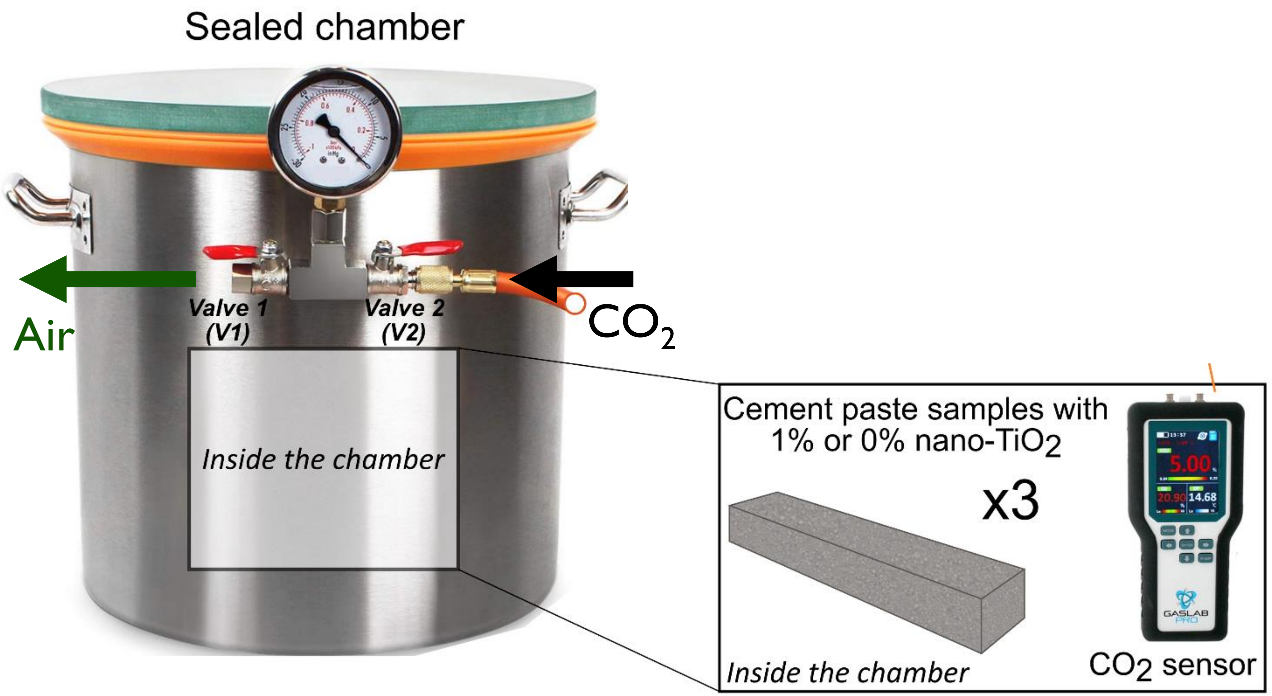
In-mold (24h)	***In-water (27d)***	***Pre-curing (24h)***
T=23±0.5°C RH=50±2%	T=25±1°C RH=100%	T=23±0.5°C RH=50±2%

To assess the effect of nano-TiO_2 addition on the CO_2 uptake

Accelerated CO_2 exposure (8h)

CO_2 *exposure*

1. **3 samples + a CO_2 sensor** are placed inside a sealed chamber



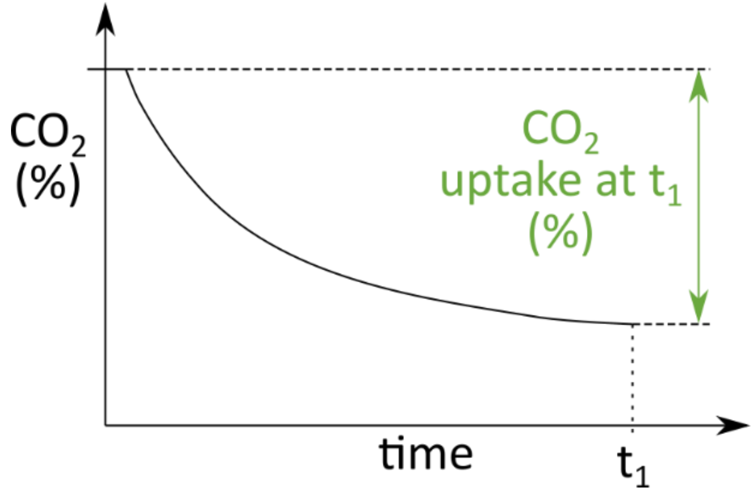
- **25% CO_2**
- **50% CO_2**
- **100% CO_2**

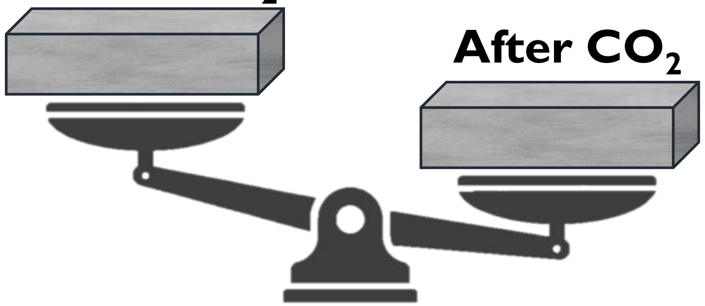
4. **8 consecutive 1-hour cycles** were performed (total of 8 hours)
5. Samples were weighted before and after

Estimation of CO_2 uptake and uptake rate

$$CO_2\ uptake(\%) = \frac{\rho_{CO_2} \cdot [V_{chamber} \cdot (\%CO_{2,start\ cycle} - \%CO_{2,end\ cycle})]}{M_{cement}} \cdot 100$$

CO_2 sensor monitoring



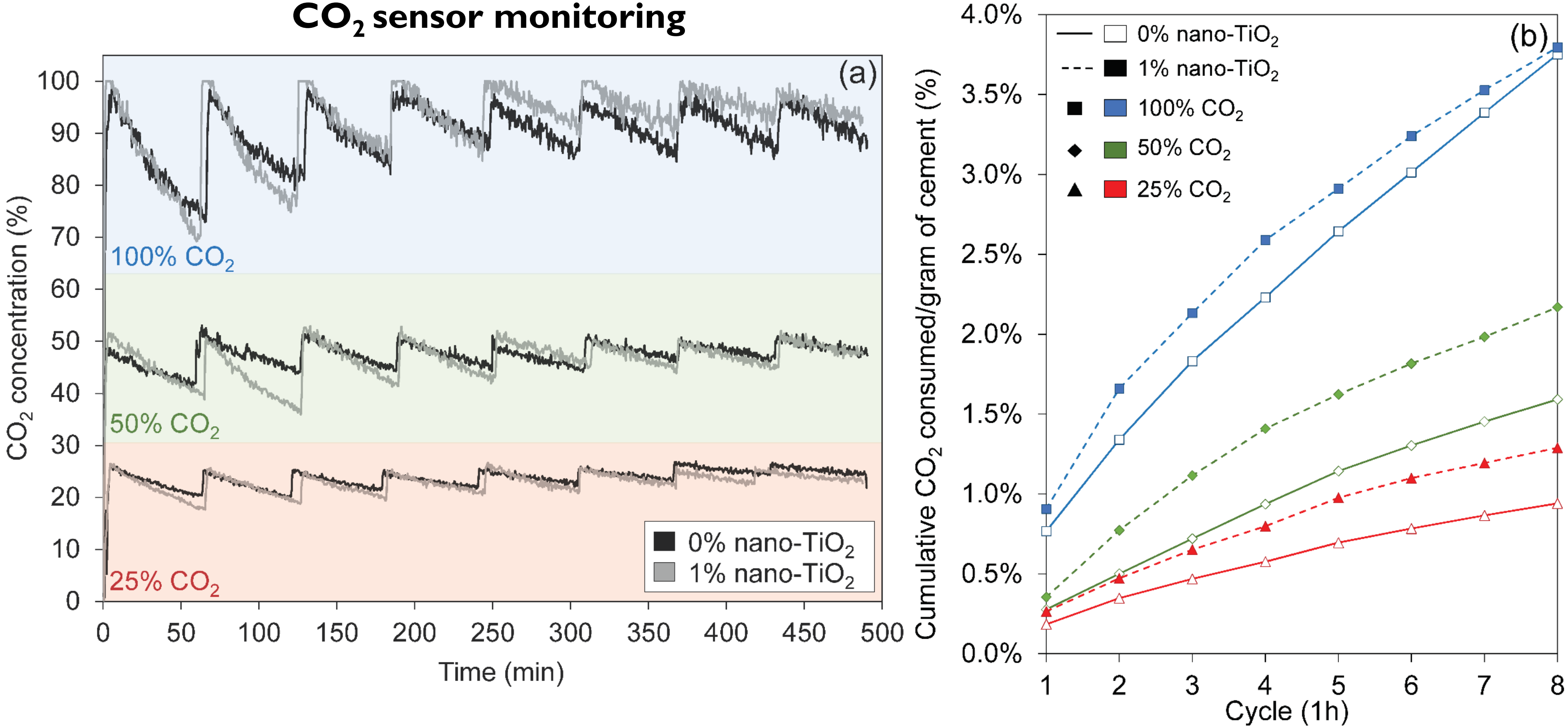


Weight method

$$CO_2\ uptake_i(\%) = \frac{M_i + \left(M_i/M_T\right) \cdot M_{water}}{M_{cement}} \cdot 100$$

3.Results

CO_2 sensor monitoring

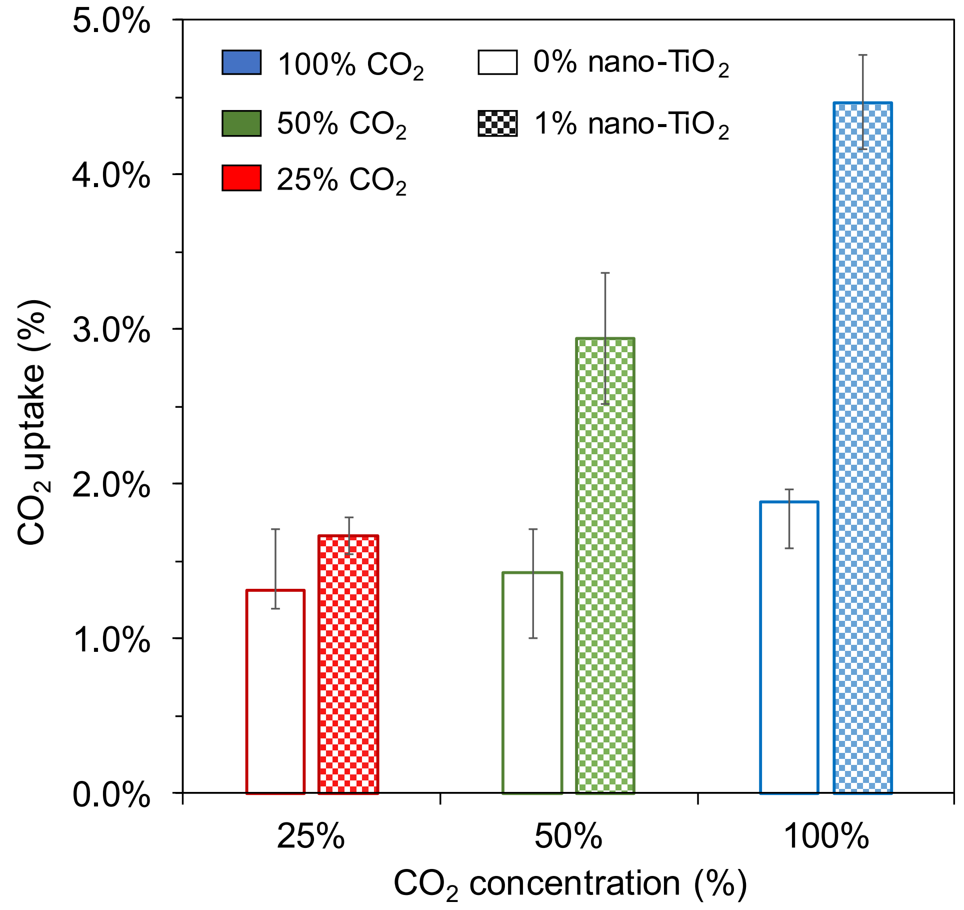


Nanomodification of the samples **enhanced carbonation** especially in **the first cycles** → reduction of surface porosity

- An increase ***CO_2 concentration*** and adding ***nano-TiO_2***, on their own enable **more CO_2 capture** at a **faster rate**

The contribution of the nano-TiO_2 to the CO_2 uptake rate is higher for lower CO_2 concentrations (25-50% CO_2) than for higher (100% CO_2).

Weight method



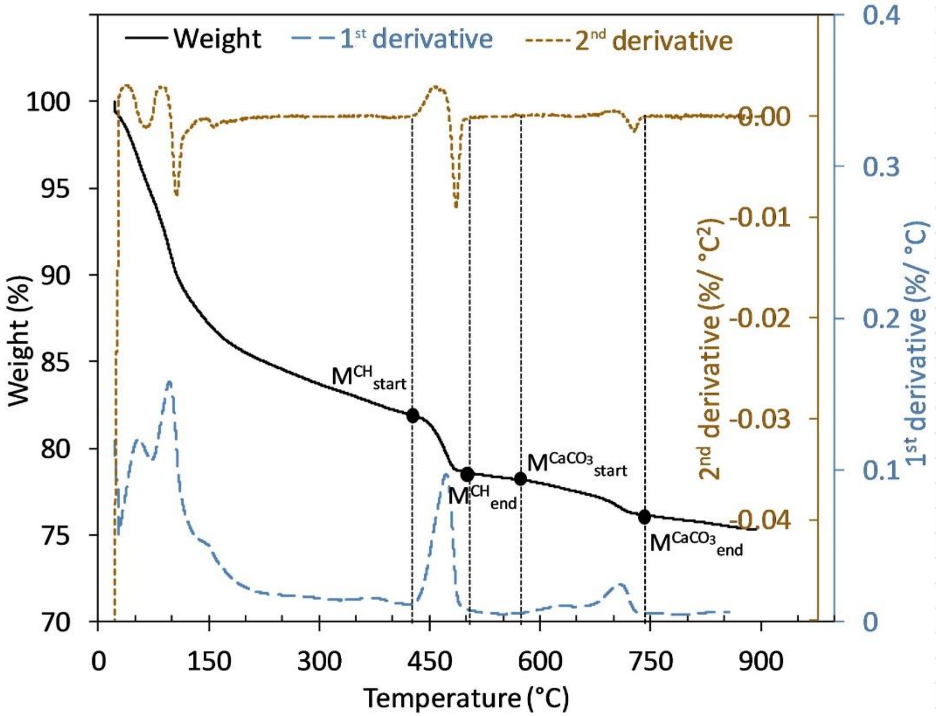
Nano-TiO_2 increased CO_2 uptake in all cases

This method may **underestimate CO_2 uptake** due to water vapor lost during chamber operations

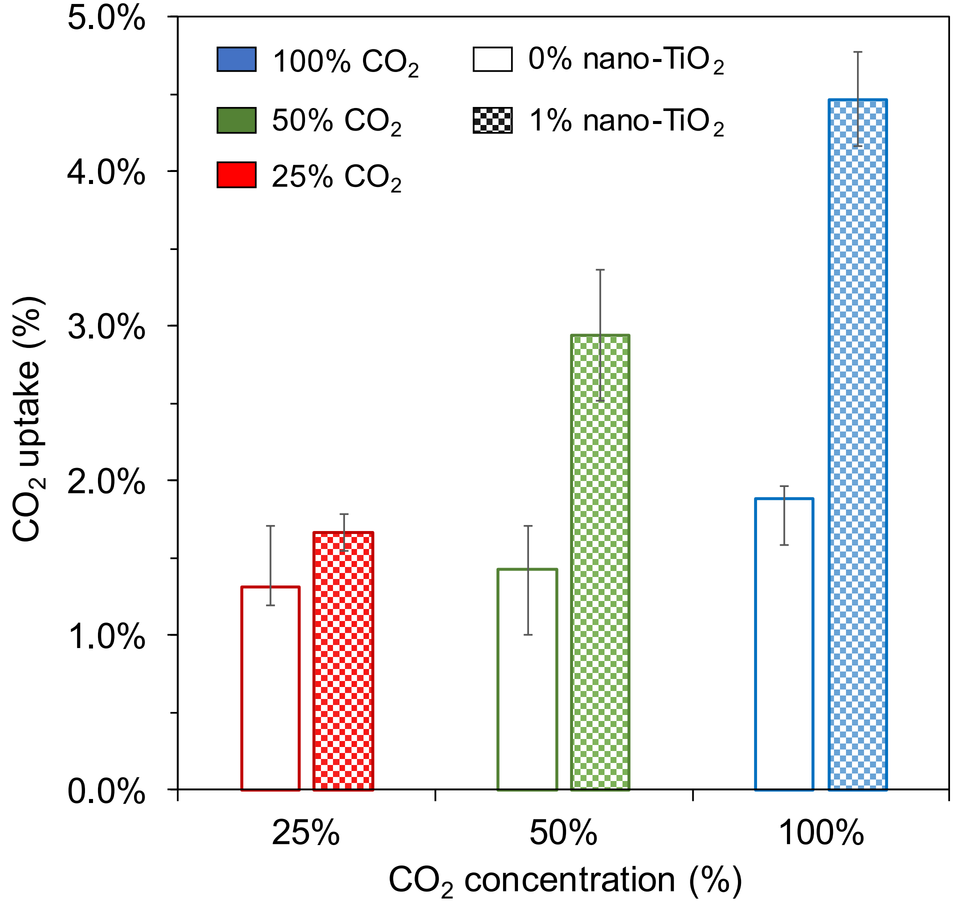
Thermogravimetric Analysis (TGA)

$$CaCO_3(g/100\,g) = 100 \cdot \frac{100.1}{44.0} \cdot \frac{1}{M_C} \cdot \left[M_{start}^{CaCO_3} - M_{end}^{CaCO_3}\right]$$

$$CO_2\ uptake(g/100\,g) = \left[CaCO_3{}^{C,sample} - CaCO_3{}^{NC,sample}\right] \cdot \frac{44.0}{100.1}$$

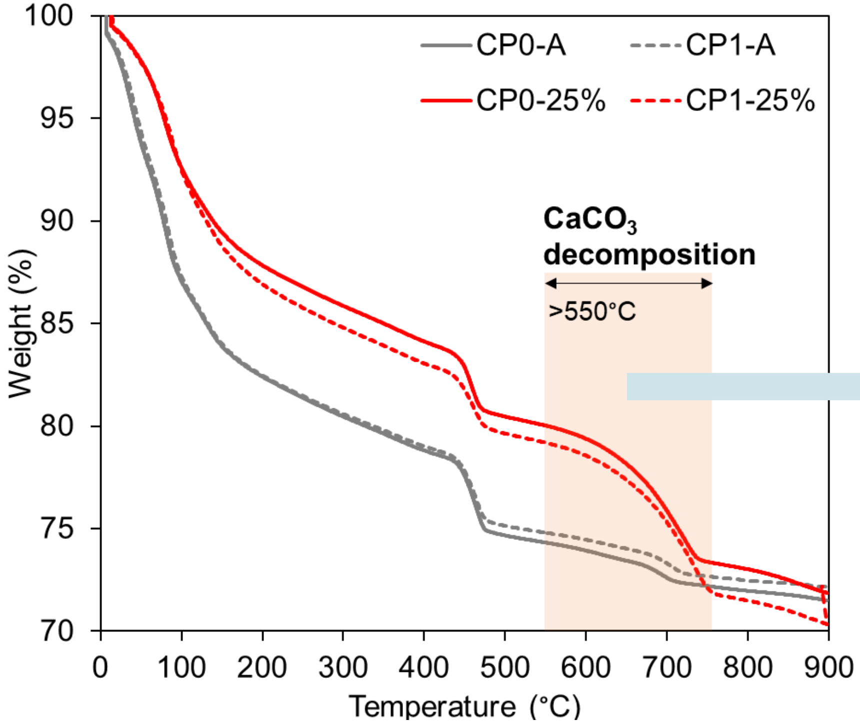


Weight method



Calcium carbonate quantification in samples unexposed and exposed to 25% CO_2

TGA



Nanomodification in samples exposed to *25% CO_2* increased **CO_2 uptake** by:

32.7%

Nano-TiO_2 increased CO_2 uptake in all cases

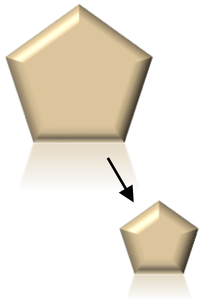
This method may **underestimate CO_2 uptake** due to water vapor lost during chamber operations

The trend of the effect of **nano-TiO_2 increasing CO_2 uptake** is consistent in all methods

?

Porosity is reduced with using nano-TiO_2 [7,11]

Reduction of CO_2 uptake → Our results are **counterintuitive**

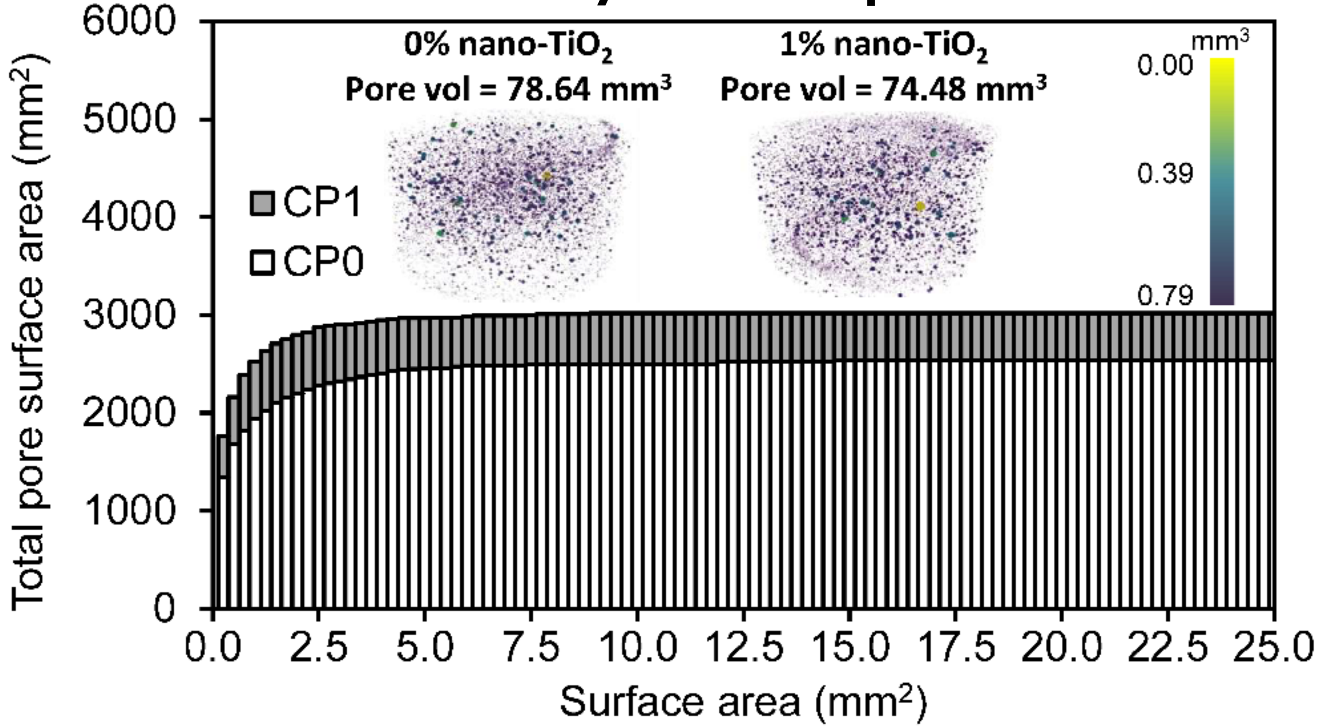


OUR PREVIOUS STUDY:

May be due to reduction of the CH crystal size with nano-TiO_2 [7]

Is there any other mechanism affecting CO_2 uptake?

3D X-Ray microscope scans



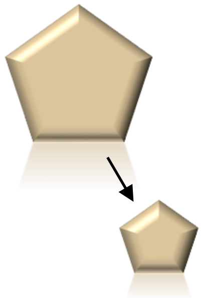
While porosity is reduced with nano-TiO_2, **pore surface area of the nanomodified samples was higher** than those without nanoparticles

- This might cause the **acceleration and increase of the carbonation** reaction observed
- Higher pore surface → more surface available for CO_2 to react

Porosity is reduced with using nano-TiO_2 [7,11]

↓

Reduction of CO_2 uptake → Our results are **counterintuitive**



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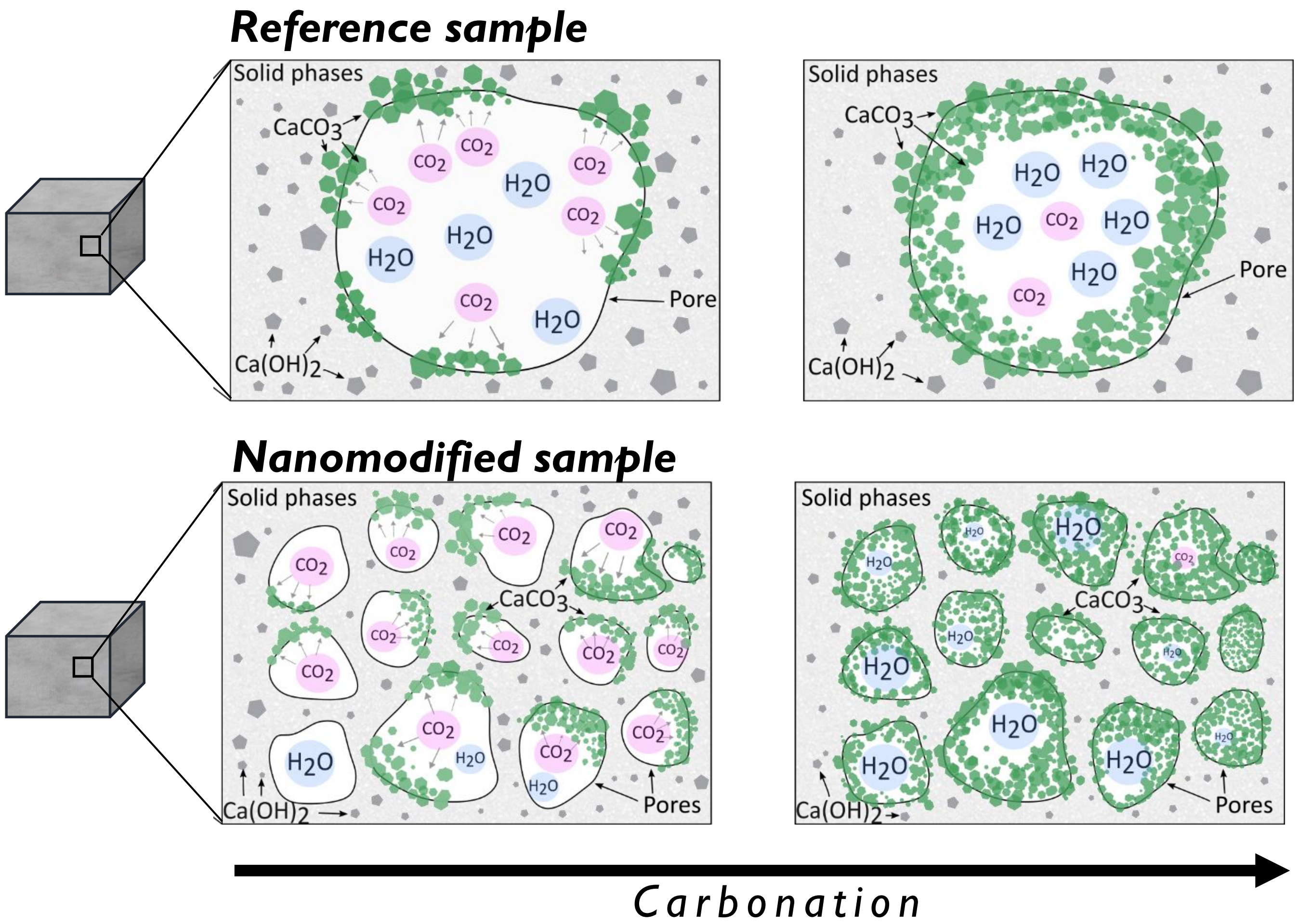

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CO_2 uptake rate estimation model

Carbonation depth: proportional to the square root of time [12]

$$CO_2\ uptake\ (g) = A\left(g/\sqrt{h}\right) \cdot \sqrt{t(h)}$$

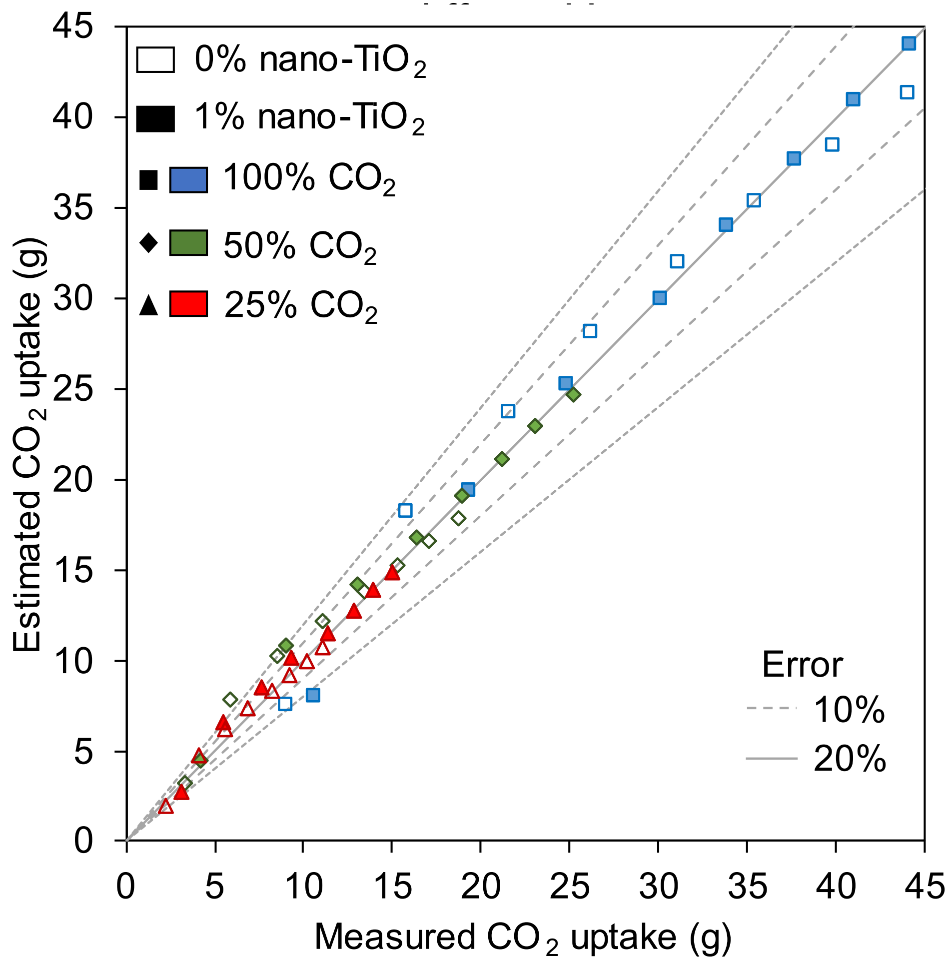
Carbonation rate coefficient

Data from results

One value of ***A*** ($g/h^{0.5}$) was estimated for each condition

Least squares method

Condition	*Nano-TiO_2 (%)*	*CO_2 (%)*
1	1	100
2	0	100
3	1	50
4	0	50
5	1	25
6	0	25



CO_2 uptake rate estimation model

Carbonation depth: proportional to the square root of time [12]

$$CO_2\ uptake\ (g) = A\left({}^{g}/_{\sqrt{h}}\right) \cdot \sqrt{t(h)}$$

Carbonation rate coefficient

Affected by:

- Nanomodification
- CO_2 concentration

Data from results

One value of ***A*** (g/h$^{0.5}$) was estimated for each condition

Least squares method

Condition	***Nano-TiO$_2$ (%)***	***CO_2 (%)***	***A (g/h$^{0.5}$)***
1	1	100	8.05
2	0	100	7.55
3	1	50	4.51
4	0	50	3.27
5	1	25	2.72
6	0	25	1.96

7% (conditions 1–2)
38% (conditions 3–4)
39% (conditions 5–6)

- Using 1% **nano-TiO$_2$ increases the carbonation rate** coefficient
- The **increase is higher for lower CO$_2$** concentrations

5. Conclusions

Main take-aways from the study

- **CO_2 uptake rate is enhanced** with the use of **nano-TiO_2** for all studied CO_2 concentrations.
- The **effectiveness of nano-TiO_2** addition in terms of CO_2 uptake rate acceleration **is higher with lower CO_2 concentrations** than with 100% CO_2.
- Even though porosity is reduced with nano-TiO_2, **pore surface area of the nanomodified samples was higher** than those without nanoparticles, which might be one of the **responsible mechanisms for the acceleration** of the CO_2 uptake.

Lopez-Arias, M., Moro, C., Francioso, V., Elgaali, H. H., & Velay-Lizancos, M. (2023). **Effect of nanomodification of cement pastes on the CO_2 uptake rate**. Construction and Building Materials, 404, 133165.

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Thank you for your attention!

ACI Concrete Convention. March 26th, 2024

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