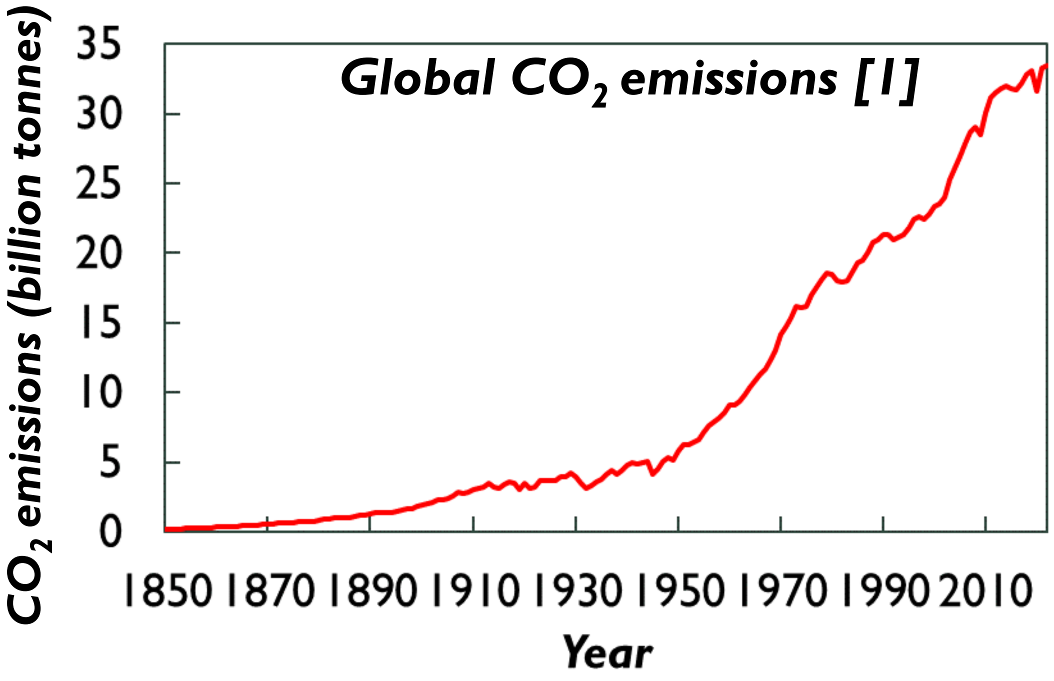
Nanomodification of Cement Paste's Microstructure and Pore Structure: Acceleration of Natural CO_2 Capture of Hardened Cementitious Composites

Marina Garcia Lopez-Arias
Carlos Moro, Ph.D.
Vito Francioso, Ph.D.
Husam H. Elgaali
Mirian Velay-Lizancos, Ph.D.

ACI Concrete Convention
Fall 2024

Table of contents

1.Introduction



Alarming CO_2 rising levels

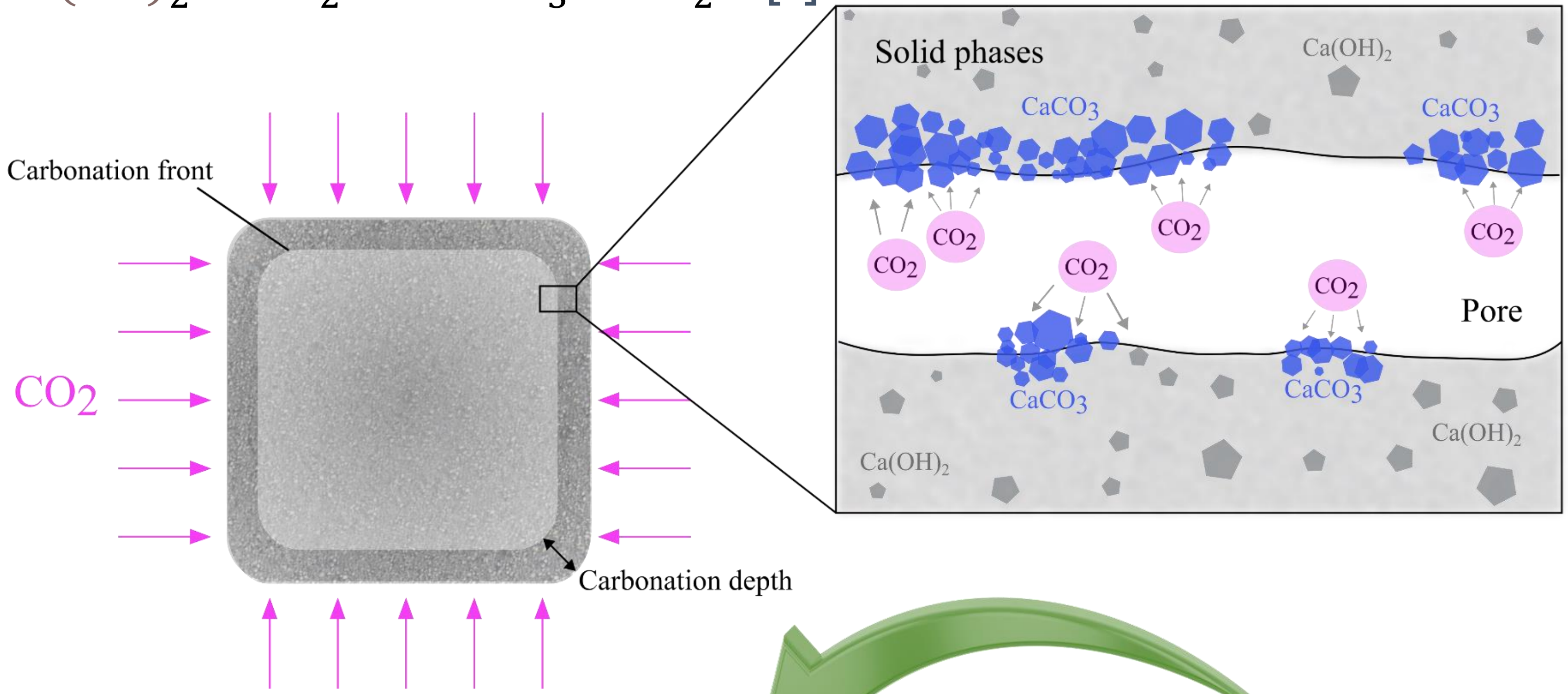
Cement manufacturing

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

What can we do?

Carbonation: *CO_2 sequestration* in cement-based materials

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



Carbonation enhancement: [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]**

Objective

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

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

2.Materials & Methods

Marina - garcial0@purdue.edu

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

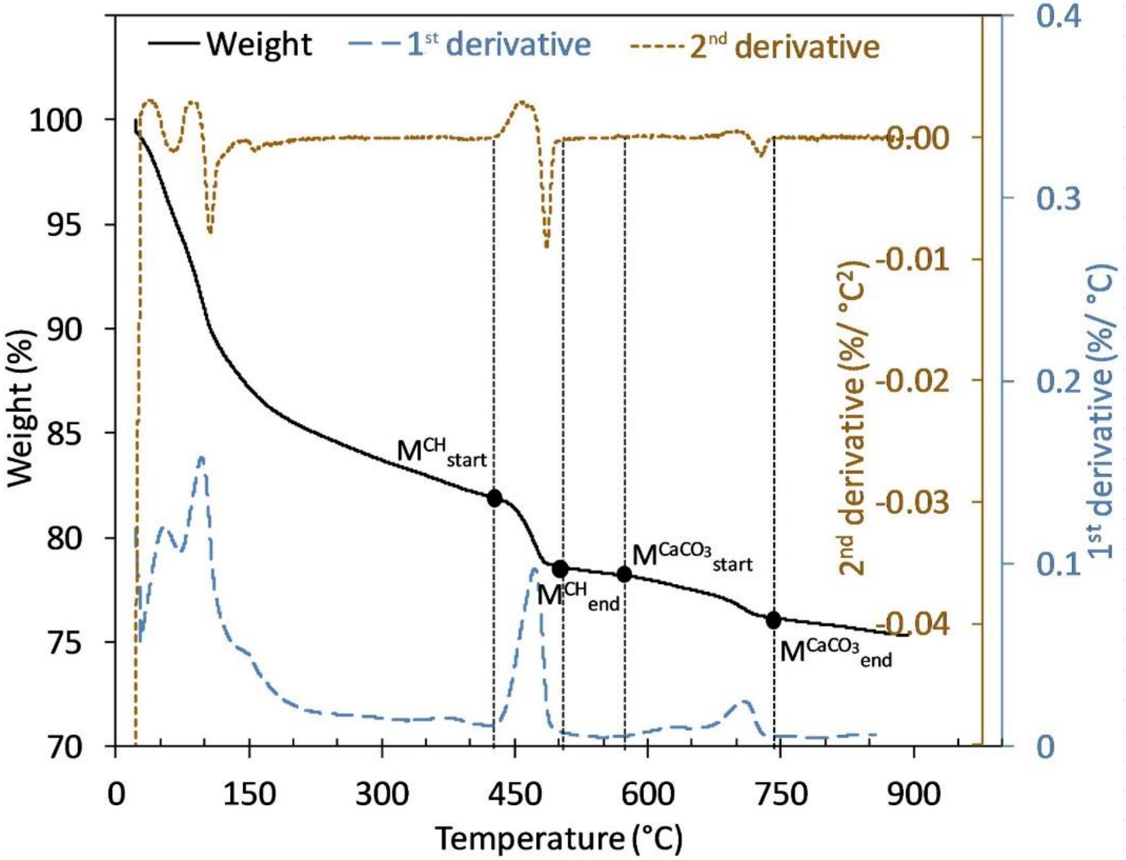
Curing procedure

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 uptake quantification



I. Thermogravimetric Analysis (TGA)

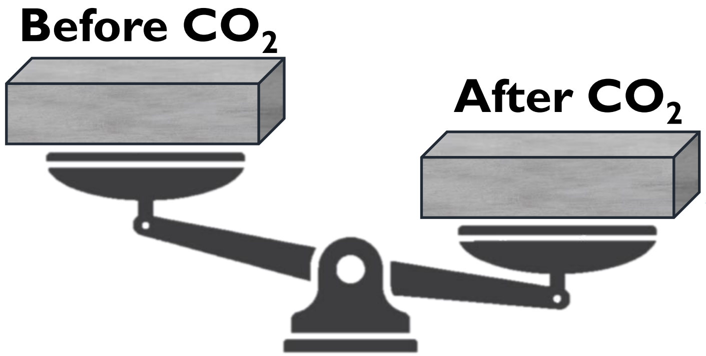
$$CaCO_3(g/100\,g) = 100 \cdot \frac{100.1}{44.0} \cdot \frac{1}{M_C} \cdot \left[M_{start}^{CaCO_3} - M_{end}^{CaCO_3}\right]$$

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

CO_2 uptake quantification

1. Thermogravimetric Analysis (TGA)

2. Weight method



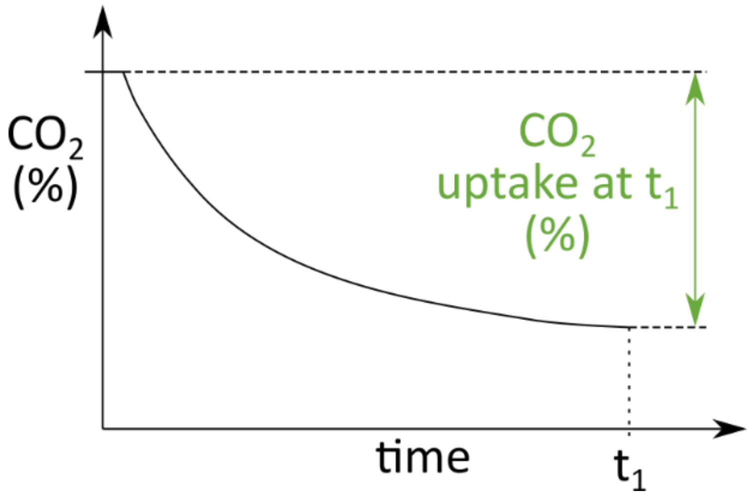
$$CO_2\ uptake_i(\%) = \frac{M_i + \left({M_i}/{M_T}\right) \cdot M_{water}}{M_{cement}} \cdot 100$$

$$\mathrm{Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O}$$

- Water is produced during the process and it needs to be correctly accounted for in order to obtain an accurate quantification

Marina - garcial0@purdue.edu

CO_2 uptake and uptake rate quantification: New method



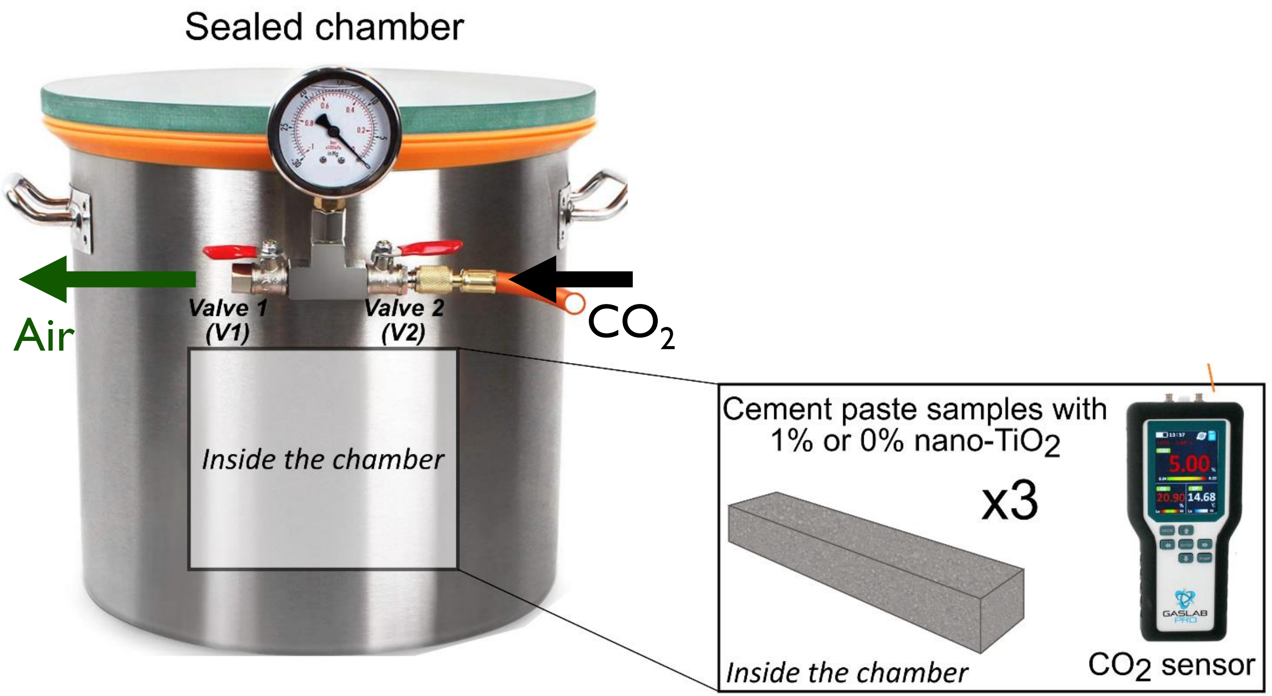
$$CO_2\,uptake(\%) = \frac{\rho_{CO_2} \cdot [V_{chamber} \cdot (\%CO_{2,start\ cycle} - \%CO_{2,end\ cycle})]}{M_{cement}} \cdot 100$$

1. Thermogravimetric Analysis (TGA)
2. Weight method
3. CO_2 sensor monitoring

Marina - *garcial0@purdue.edu*

CO_2 exposure test

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



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

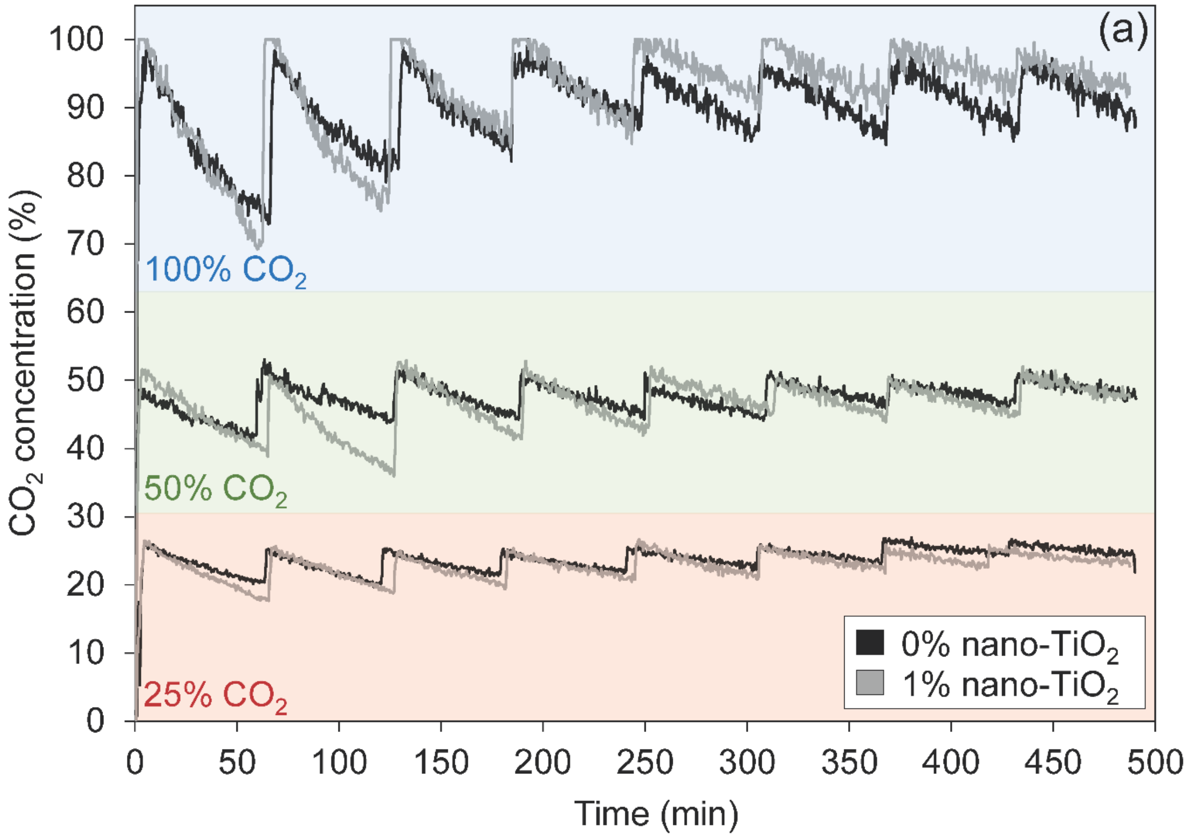
4. **8 consecutive 1-hour cycles** were performed (total of 8 hours)
5. Samples were weighted before and after

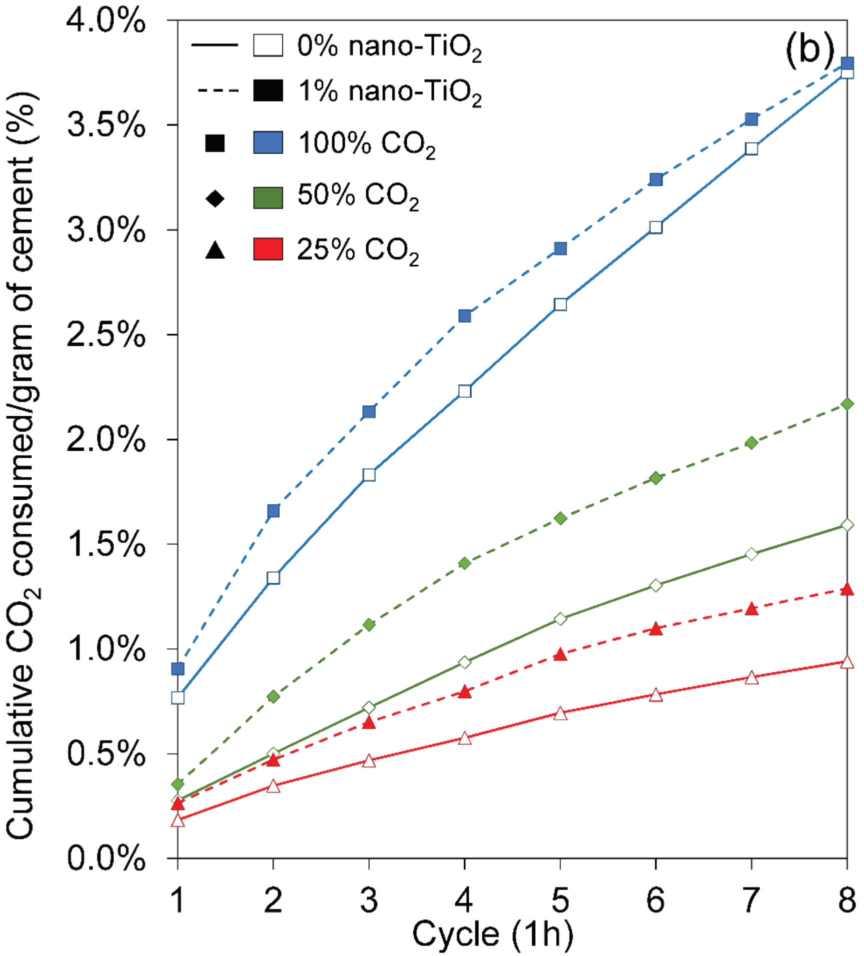
Marina - *garcial0@purdue.edu*

3.Results

Marina - *garcial0@purdue.edu*

CO_2 sensor monitoring



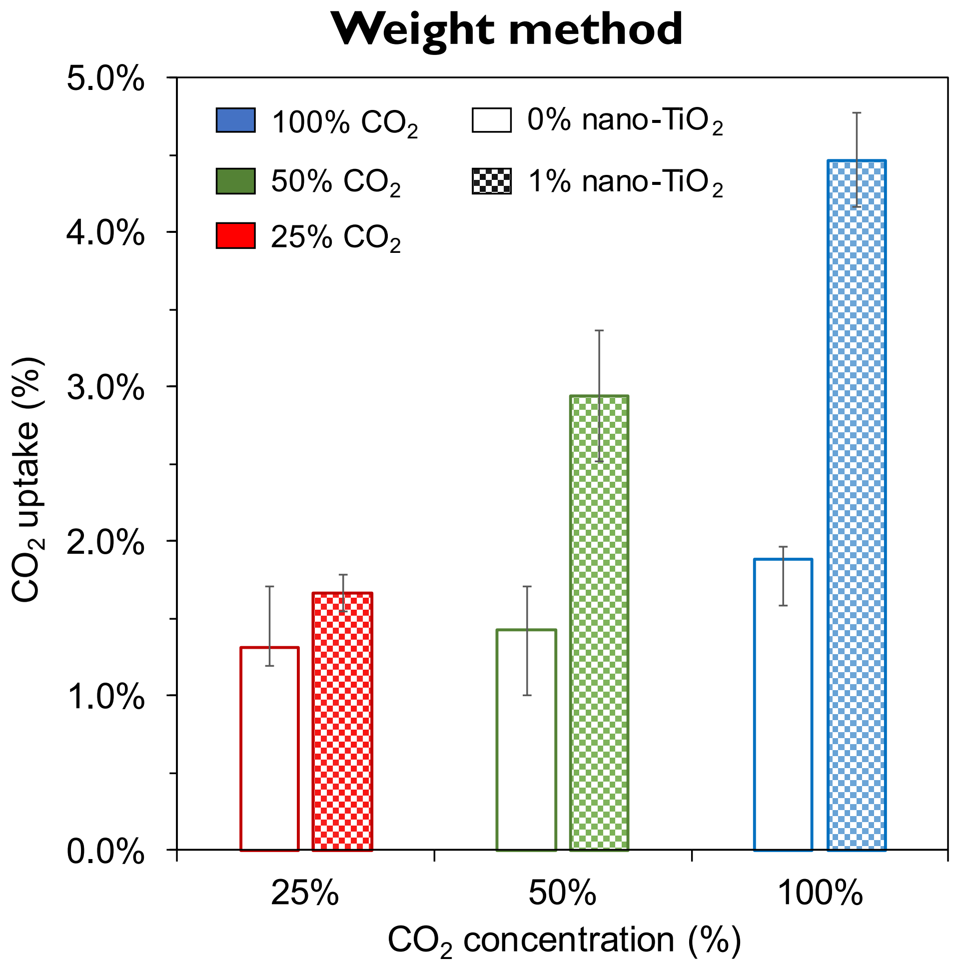


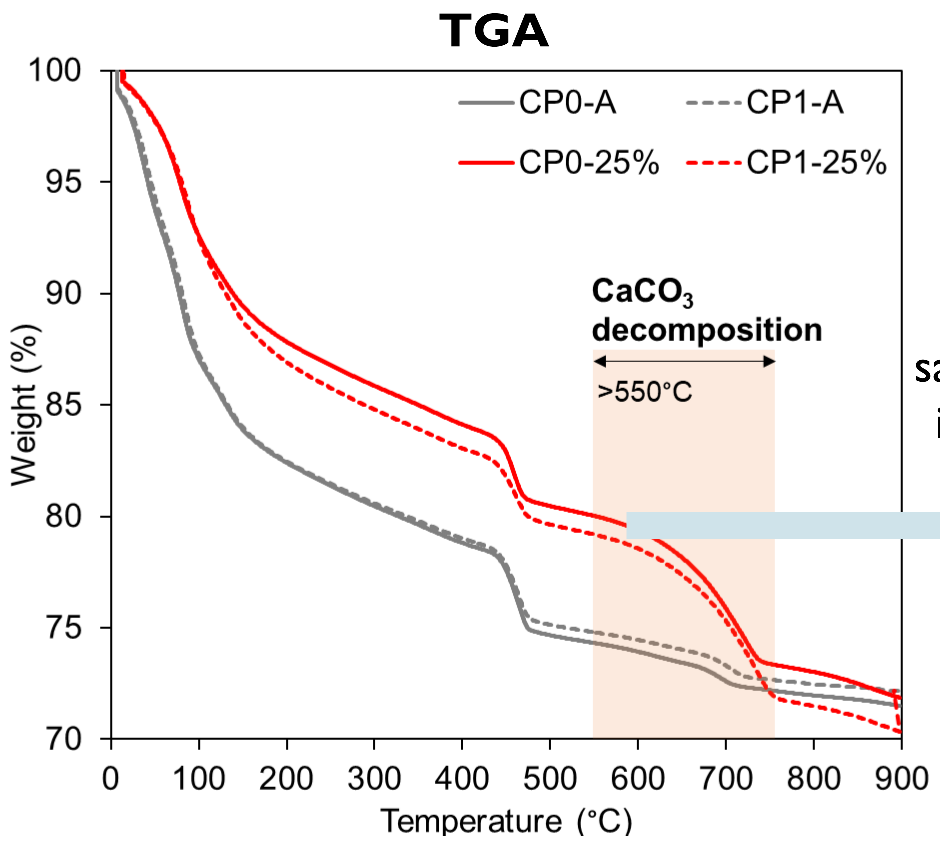
Nanomodification of the samples **enhanced carbonation** especially in **the first cycles** → reduction of surface porosity

- 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).

Marina - *garcial0@purdue.edu*





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

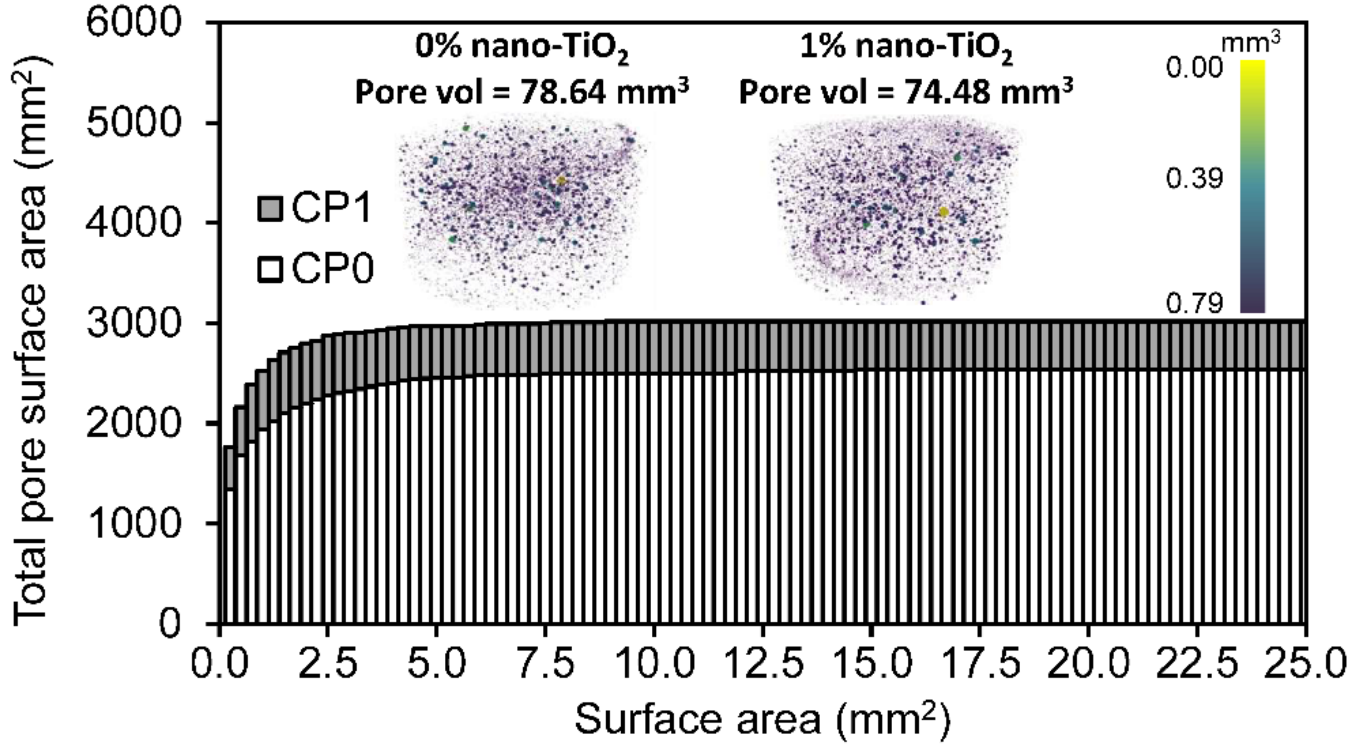
Porosity is reduced with using nano-TiO_2 [7,11]

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



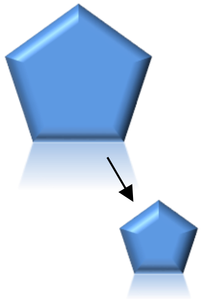
While porosity is reduced with nano-TiO_2, **pore surface area of the nanomodified samples was higher** than those without nanoparticles

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

Marina - garcial0@purdue.edu

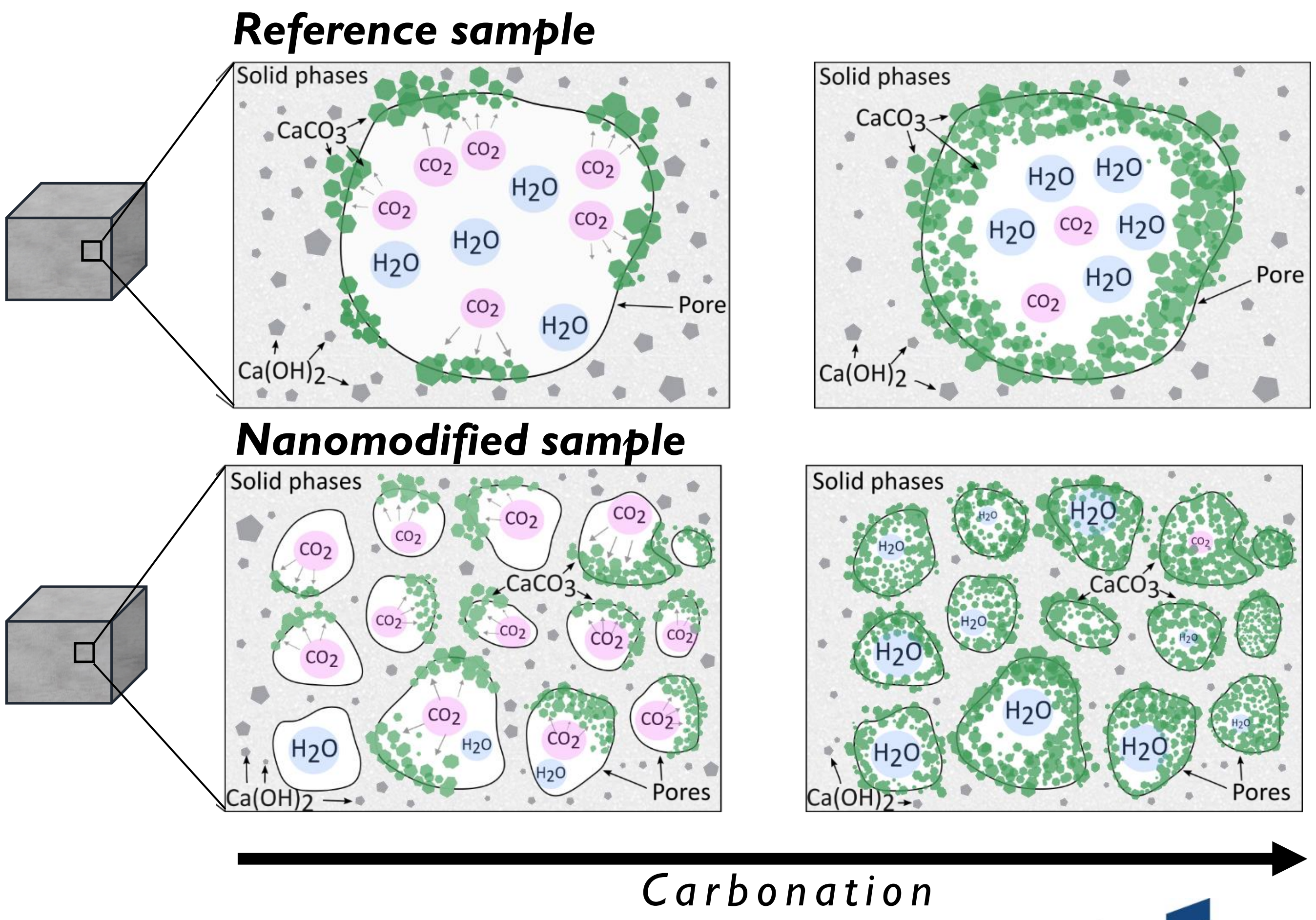
Porosity is reduced with using nano-TiO_2 [7,11]

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?



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

Marina - garcial0@purdue.edu

CO_2 uptake rate estimation model

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

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

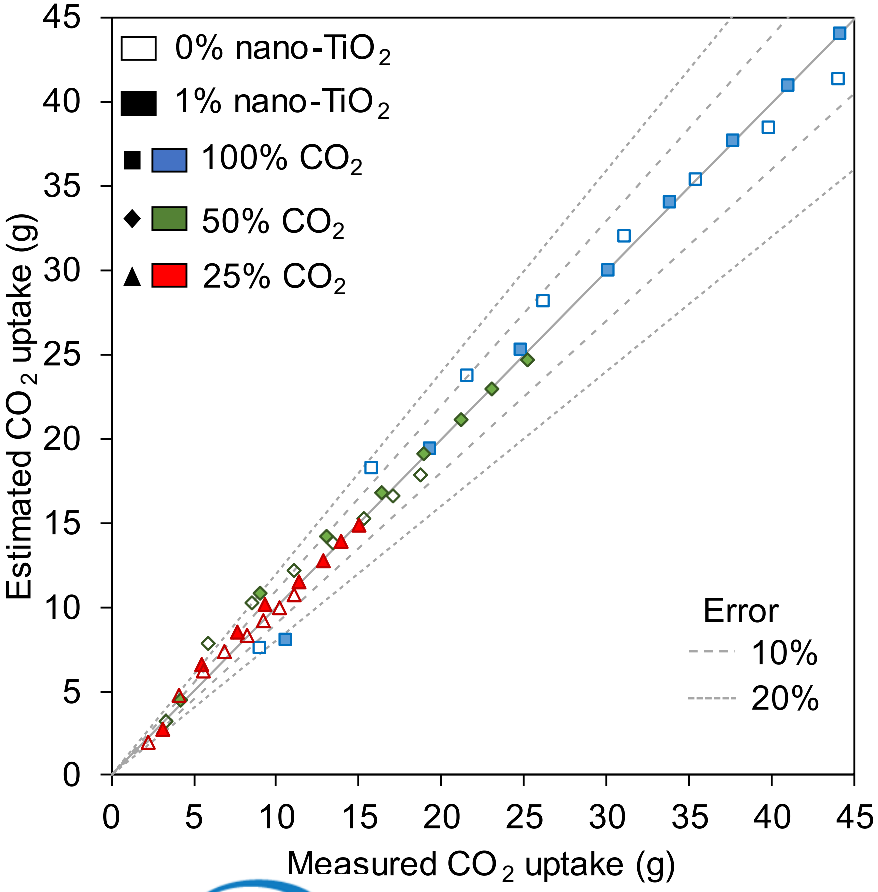
Carbonation rate coefficient

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



Marina - *garcial0@purdue.edu*

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.

REFERENCES

[1] H. Ritchie and M. Roser, "Renewable Energy - Our World in Data." Accessed: Feb. 22, 2022. [Online]. Available: https://ourworldindata.org/renewable-energy

[2] N. Mahasenan, S. Smith, and K. Humphreys, "The cement industry and global climate change: current and potential future cement industry CO2 emissions," Elsevier, Accessed: Sep. 06, 2021. [Online]. Available: https://www.sciencedirect.com/science/article/pii/B9780080442761501574

[3] B. Šavija and M Luković, "Carbonation of cement paste: Understanding, challenges, and opportunities," Constr Build Mater, 2016, Accessed: Apr. 13, 2022. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0950061816306936

[4] M. Bertos, S. Simons, C. Hills, and PJ Carey, "A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO2," J Hazard Mater, 2004.

[5] D. Sharma and S Goyal, "Accelerated carbonation curing of cement mortars containing cement kiln dust: An effective way of CO2 sequestration and carbon footprint reduction," J Clean Prod, 2018, Accessed: Sep. 06, 2021. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0959652618313532

[6] V. Rostami, Y. Shao, and AJ Boyd, "Carbonation curing versus steam curing for precast concrete production," Journal of Materials in Civil Engineering, vol. 24, no. 9, pp. 1221–1229, Sep. 2012, doi: 10.1061/(ASCE)MT.1943-5533.0000462.

[7] C. Moro, V. Francioso, and M. Velay-Lizancos, "Modification of CO2 capture and pore structure of hardened cement paste made with nano-TiO2 addition: Influence of water-to-cement ratio and CO2," Journal of Construction and Building Materials, 2021, Accessed: Sep. 06, 2021. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0950061820341349

[8] M. Safiuddin, M. Gonzalez, J. Cao, and S. L. Tighe, "State-of-the-art report on use of nano-materials in concrete," International Journal of Pavement Engineering, vol. 15, no. 10, pp. 940–949, Nov. 2014, doi: 10.1080/10298436.2014.893327.

[9] L Cassar, "Photocatalysis of cementitious materials: clean buildings and clean air," MRS Bull, vol. 29, no. 5, 2004, Accessed: Sep. 06, 2021. [Online]. Available: https://www.cambridge.org/core/journals/mrs-bulletin/article/photocatalysis-of-cementitious-materials-clean-buildings-and-clean-air/9BB0557274134CE41738C6EA1D341D53

[10] B. Ma, H. Li, J. Mei, X. Li, and F Chen, "Effects of Nano-TiO2 on the Toughness and Durability of Cement-Based Material," Advances in Materials Science and Engineering, 2015, Accessed: Jul. 30, 2023. [Online]. Available: https://www.hindawi.com/journals/amse/2015/583106/

[11] J. Chen, S. Kou, and C Poon, "Hydration and properties of nano-TiO2 blended cement composites," Cem Concr Compos, 2012, Accessed: Feb. 23, 2023. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0958946512000364

[12] Ho, D. W. S., & Lewis, R. K. (1987). Carbonation of concrete and its prediction. Cement and Concrete Research.

Thank you for your attention!

ACI Concrete Convention. Fall 2024

Marina Garcia Lopez-Arias
Carlos Moro, Ph.D.
Vito Francioso, Ph.D.
Husam H. Elgaali
Mirian Velay-Lizancos, Ph.D.

garcial0@purdue.edu

Connect with me!