



# Influence of nanoCaCO<sub>3</sub> seeding on the hydration and carbonation behavior of MgO based cements



Jaime Madrideo Varela<sup>1</sup>, Ala Douba<sup>2</sup>, Shiho Kawashima<sup>2</sup>

<sup>1</sup>Department of Applied Physics & Applied Mathematics, Columbia University, New York, NY 10027

<sup>2</sup>Department of Civil Engineering & Engineering Mechanics, Columbia University, New York, NY, 10027

## Background & Motivation

Reject brine from desalination plants is typically discharged into the ocean, posing environmental concerns by having concentrations of ions five times greater than seawater as well as other harmful constituents from treatment. It is possible to extract resources of interest that can be processed into valuable resources. Mg(OH)<sub>2</sub> is extracted from brine via addition of NaOH and can be calcinated at ~500°C to produce reactive MgO. This material is used in the production of reactive MgO cements (RMC) that have the potential of replacing industry standard Ordinary Portland Cement (OPC), given its comparable properties and more sustainable production. CaCO<sub>3</sub> can also be precipitated from brine through the addition of NaOH and bubbling of CO<sub>2</sub>. This has potential to be used as a nucleation seed in cement which can promote hydration and carbonation and consequently enhance its properties.

RMCs can harden and gain strength through CO<sub>2</sub> curing, where the material "soaks up" CO<sub>2</sub> to form solid carbonates. Under ambient conditions MgO reacts with water, i.e. undergoes hydration, to produce Mg(OH)<sub>2</sub> which leads to setting. Under carbonation, the Mg(OH)<sub>2</sub> reacts with CO<sub>2</sub> and forms hydrated magnesium carbonates (HMC), which densifies and cements the structure to lead to strength gain.

Some materials used as nucleation seeds like hydromagnesite have been proven to enhance RMCs properties<sup>1</sup>. Others like nanoCaCO<sub>3</sub> have only been shown to work with OPC<sup>2</sup>. As we can extract CaCO<sub>3</sub> and MgO from reject brine, this project is focused on the influence of nanoCaCO<sub>3</sub> seeding on the hydration and carbonation of RMCs.

## Materials & Procedures

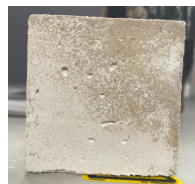
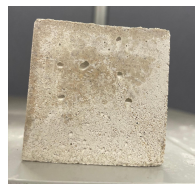
- Materials:
  - Water
  - Sand (aggregate)
  - MgO (binder)
  - nanoCaCO<sub>3</sub> (seed)

Mass ratios

	Water	Sand	MgO	nanoCaCO <sub>3</sub>
Mix 1	0.9	2	1	0
Mix 2	0.9	2	0.95	0.05

- Mix Design:
  - 1. Control
  - 2. 5% nanoCaCO<sub>3</sub> replacement by weight

- Samples:
  - 2in cubes (x2 for each)
  - Air curing (0-24h, 25°C, room conditions)
  - Carbon curing (Day 1-28, 20% CO<sub>2</sub>, 25°C, 80% RH)

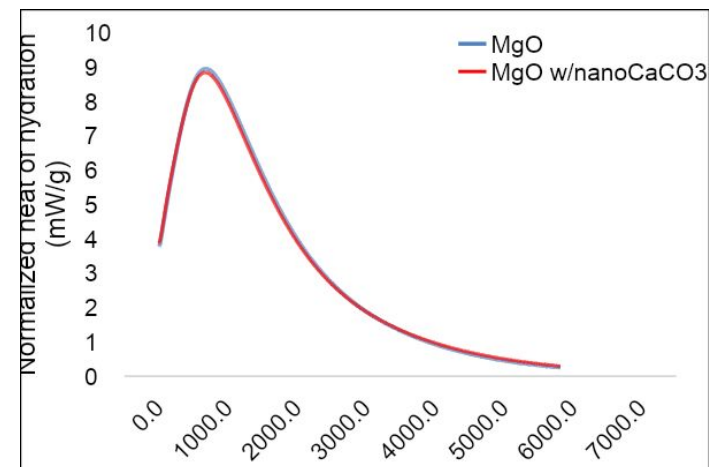


## Testing

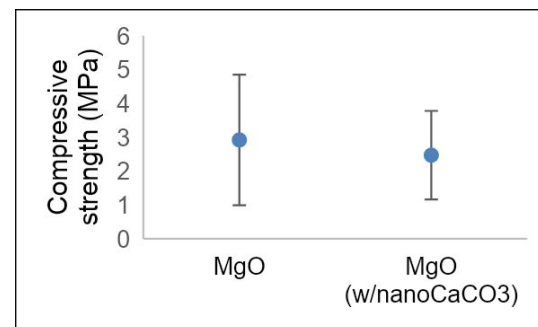
We can measure and compare the degree of hydration and carbonation through three tests to determine the influence of nanoCaCO<sub>3</sub> seeding.

- Isothermal Calorimetry: Measure of heat flow over 72h, indicator of kinetics and degree of hydration
- Strength testing: Indirect measure and direct assessment of the effectiveness of carbon curing. Representative strength taken from sample average
- Thermogravimetric analysis (TGA): Measures thermal decomposition of phases through mass loss, potential indicator of degree of carbonation via quantifying the amount of carbonate phases

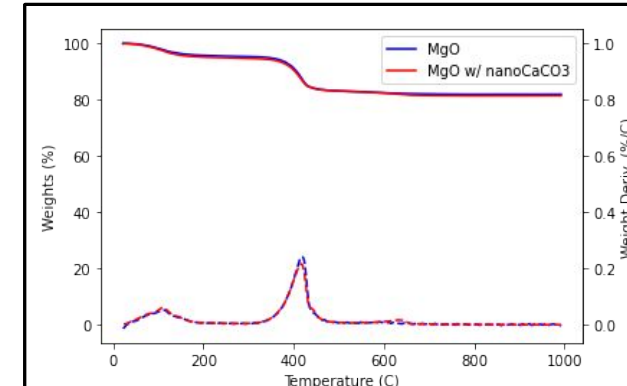
## Isothermal Calorimetry



## Strength Testing



## Thermogravimetric Analysis (TGA)



## Conclusion & Discussion

In this project, we set out to investigate the influence of nanoCaCO<sub>3</sub> seeds on the behavior of reactive magnesium cement. We expect seeding to improve the kinetics, degree of hydration and carbonation of RMCs, leading to enhanced strength. Our results suggest that nanoCaCO<sub>3</sub> is not a good seed for this type of cement. The isothermal calorimetry shows very little difference between the two samples, meaning that the nanoCaCO<sub>3</sub> had little to no impact on the degree of hydration or the kinetics. In terms of strength, plain MgO had a representative strength that was 18.2% higher than MgO w/ nanoCaCO<sub>3</sub>. Finally, there was also little difference in the TGA curves that show similar degree of hydration and carbonation. The peak at ~100C corresponds to water and HMC, the peak at 400 C is for brucite and the peak at >500 C is for HMC. This suggests that plain MgO had a higher degree of hydration but slightly lower carbonation.

In the end, using nanoCaCO<sub>3</sub> in magnesium based cements does not improve its resulting properties. Clearly, we would need to further our research to fully determine the usefulness of this seed. Perhaps by increasing CO<sub>2</sub> content or increasing replacement amounts of nanoCaCO<sub>3</sub> can produce a cement comparable to OPC.

## References

- Unluer, C., & Al-Tabbaa, A. (2013). Impact of hydrated magnesium carbonate additives on the carbonation of reactive MgO cements. *Cement and Concrete Research*, 54, 87-97.
- Sato, T., & Beaudoin, J. J. (2019). Effect of nano-CaCO<sub>3</sub> on hydration of cement containing supplementary cementitious materials. In *ICE Themes Low Carbon Concrete* (pp. 231-248). ICE Publishing.
- Ma, S., Akca, A. H., Esposito, D., & Kawashima, S. (2020). Influence of aqueous carbonate species on hydration and carbonation of reactive MgO cement. *Journal of CO<sub>2</sub> Utilization*, 41, 101260.

## Acknowledgements

Thanks to Palash Badjatya for helping with TGA testing. Special thanks to Prof. Yin Yip and Peter Cruz (SEAS'22) for the work done on the UAE Brine management challenge.