

# Carbonation Before Curing: A New Path to Concrete Sustainability



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## Concrete as a Carbon Sink

Concrete is the most consumed material in the world after water [1]. The concrete and cement industries are taking steps to dampen the carbon footprint of their respective materials. For instance, the Global Cement and Concrete Association and member companies have committed to producing carbon neutral concrete by 2050 [2]. Similarly, The Portland Cement Association released a roadmap to carbon neutrality by 2050 [3], and the National Ready Mixed Concrete Association joined the aforementioned GCCA initiative [4].

Hardened concrete serves as a natural carbon sink, an intrinsic material property that can be essential to reducing its carbon emissions if properly understood and leveraged. It does so by carbonating hydration products (mainly calcium hydroxide) during its use phase and end-of-life. This natural carbon uptake also increases the compressive strength of cement-based products, but can impact their corrosion resistance, which must be carefully considered for steel-reinforced concrete [a].

There are ongoing efforts to induce early-stage carbonation through forced carbonation, in which the amount of  $\text{CO}_2$  gas present when concrete undergoes early-stage hydration is artificially increased. While forced carbonation can, in some cases, improve strength and reduce water absorption, this process demands sophisticated procedures and is best applied to precast concrete elements produced in artificially  $\text{CO}_2$ -rich environments [4].

To address the current limitations of forced carbonation and other carbon capture, uptake, and storage (CCUS) technologies, the MIT CSHub has developed a framework to store  $\text{CO}_2$  in concrete through **chemically induced pre-cure carbonation (CIPCC)**, in which  $\text{CO}_2$  is introduced into a concrete mix in the form of a solid powder (sodium bicarbonate; see Figure 1 on the next page) instead of a gas.

In addition to being convenient for cast-in-place applications, **CIPCC allows for the storage of a controlled and precise quantity of  $\text{CO}_2$  in concrete.**

## Key Takeaways:

- CSHub suggests a new way of sequestering  $\text{CO}_2$  in concrete through chemically induced pre-cure carbonation (CIPCC).
- CIPCC can theoretically make concrete's uptake capacity sufficient to offset at least 40% of the emissions from the calcination of cement.
- CIPCC can improve concrete's early-stage mechanical performance due to accelerated hydration reactions.
- Chemical reactions that take place during CIPCC can be understood using techniques like Raman spectroscopy, micro-indentation, and thermogravimetric analysis.



From buildings to pavements, concrete has a dynamic, evolving relationship with its environment, as exemplified by properties like its carbon uptake.

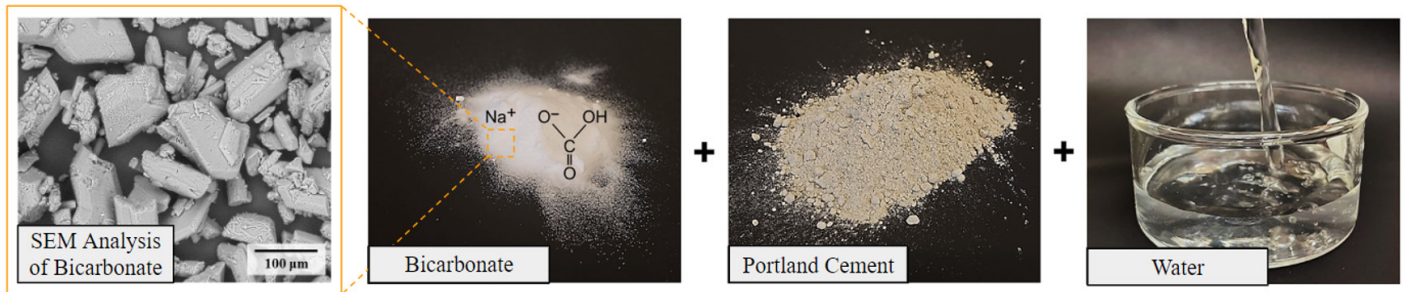


Figure 1. Carbonated samples were produced by mixing alite ( $C_3S$ ), the most reactive component of OPC, with solid sodium bicarbonate crystals and water. This differs from many previous applications which used gaseous  $CO_2$  when trapping carbon dioxide in concrete. Naturally, the mix used here can be further applied to traditional mortars and concrete by adding aggregates and replacing alite with OPC, as shown in Figure 1 above.

Furthermore, this method facilitates an additional mechanism of  $CO_2$  storage in concrete by building on previous CSHub work on amorphous hydration phases; these phases were also shown to carbonate via CIPCC [5], [b].

While the ability of concrete to sequester  $CO_2$  after curing (both through natural and forced carbonation) is well-documented, little is known regarding the specific phase transformations that occur in pre-cure carbonation, the role of amorphous phases, or the mechanical consequences of these reactions.

To address these unanswered questions, an extensive laboratory program was run by the CSHub incorporating techniques like Raman spectroscopy, micro-indentation and thermogravimetric analysis (TGA). The findings of this program are summarized in this brief.

## Analysis of Chemo-mechanical Properties

To understand the mechanisms of pre-cure carbonation reactions, the chemomechanics of cement carbonation were studied over time scales ranging from one hour to several days. A model system was developed that partially substituted alite with sodium bicarbonate, which reacts with cement and water to introduce  $CO_2$  into the concrete mix. Cementitious samples were created consisting of 0% (the control sample), 5%, 10%, 15%, and 20% sodium bicarbonate by weight, resulting in different levels of

carbonation (here, the amount of  $CO_2$  present in the cured sample and in different forms).

**Micro-indentation**, a process which can extrapolate a material's elastic and mechanical properties on a micron scale, was used to determine the hardness of the carbonated samples. As shown in Figure 2, during the early stages of

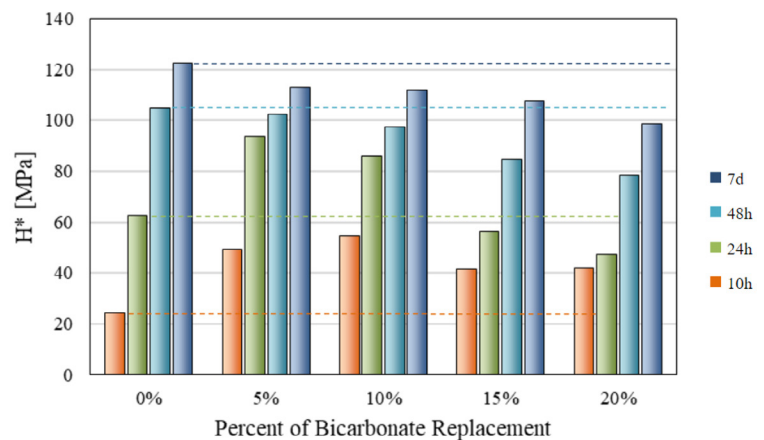


Figure 2. Time evolution of the specific hardness ( $H^*$ ) in bicarbonate-substituted cements. Carbonated samples display a nucleating or 'seeding' effect during early hydration caused by increased levels of C-S-H in the concrete which strengthens the material.

hydration (the first 10 hours), all of the carbonated samples exhibited significantly higher specific hardness compared to the uncarbonated control sample. The force-displacement curves in Figure 3 also show that moderate levels of carbonation allow samples to withstand more force after 24 hours of hydration. It was found that this increased strength of pre-cure carbonated concrete is caused by calcium

carbonate polymorphs. These carbonates act as nucleation sites for the formation of C-S-H, the primary phase of concrete that binds its components together, allowing the material to hydrate and cure more quickly.

As seen in Figure 2, the control sample slightly mechanically outperformed its carbonated equivalents after seven days, but there was no statistical difference in hardness for samples up to 15% sodium bicarbonate. Therefore, 15% replacement of cement with bicarbonate was established as a practical limit that optimizes carbon storage without compromising the concrete's strength.

Additionally, **Raman microscopy** was used to track how these carbonate phases transform and nucleate C-S-H production. Raman microscopy allows for a material's molecular structure to be observed, including its amorphous and transient components that cannot be analyzed with other techniques typically used in concrete chemistry research.

Using the technique to evaluate the structure of carbonated samples over time, the CSHub researchers revealed the presence of carbonates (such as calcite, vaterite and ikaite) which were integrated into the structure along with cement phases typically found in

regular concrete (alite, C-S-H and portlandite). Figure 4 shows how these carbonates are present in carbonated samples, but not in the reference sample during early-stage hydration.

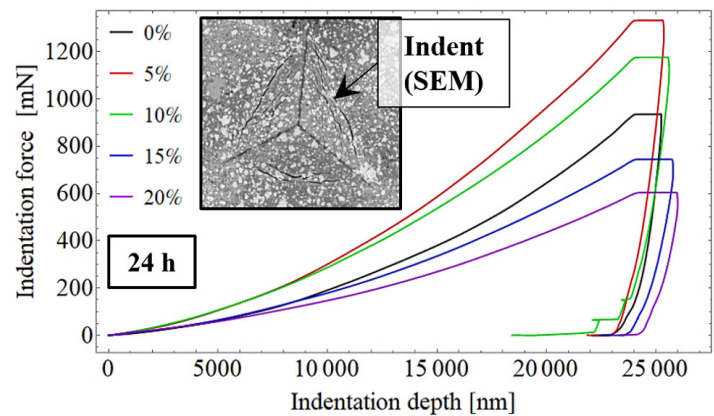


Figure 3. Force-Displacement curves from micro-indentation after 24 hours of hydration show increased strength in 5% and 10% bicarbonate-substituted samples, and no statistical difference in the 15% sample vs. the control.

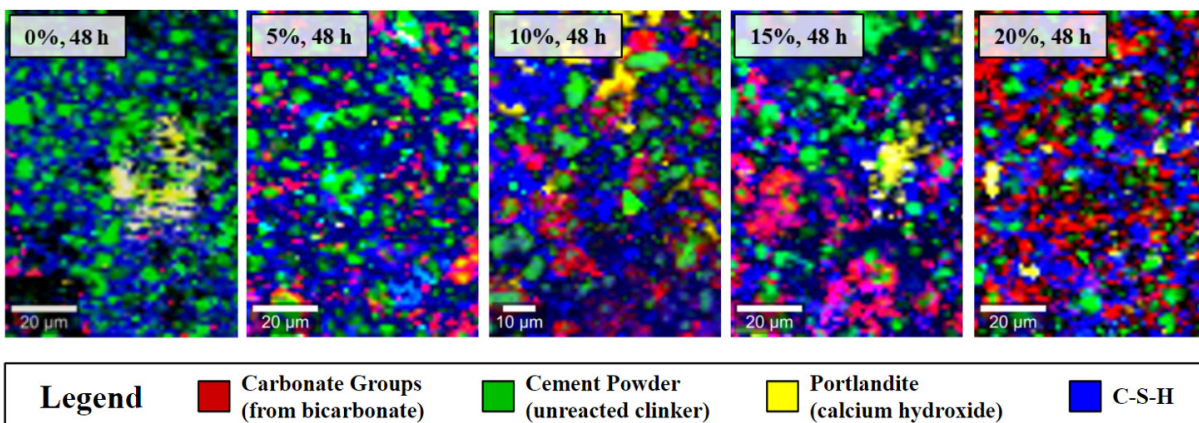


Figure 4. Raman maps of control and carbonated concrete samples after 48 hours of hydration along with their hydration products. Only the carbonated samples have carbonate groups (red), which can appear pink in color when intermixed with the blue C-S-H groups.



To confirm that the amount of carbonates in concrete scales with the level of bicarbonate substitution, the area-fraction of carbonates visible in Raman maps was calculated. As seen in Figure 4, no carbonates are present in the control sample, and the percentage of the Raman map containing carbonate regions increases as more bicarbonate is added. A technique called **thermogravimetric analysis (TGA)** was used to corroborate these results [c]. Furthermore, microstructural characterization of Raman maps in Figure 4 using correlation functions revealed that C-S-H in carbonated samples formed faster than in control samples, and that the C-S-H and carbonates precipitated together. This demonstrates how the carbonates introduced through early-stage pre-cure carbonation may nucleate the formation of C-S-H, and how this nucleation may allow C-S-H to form more quickly in carbonated concrete (see Figure 6).

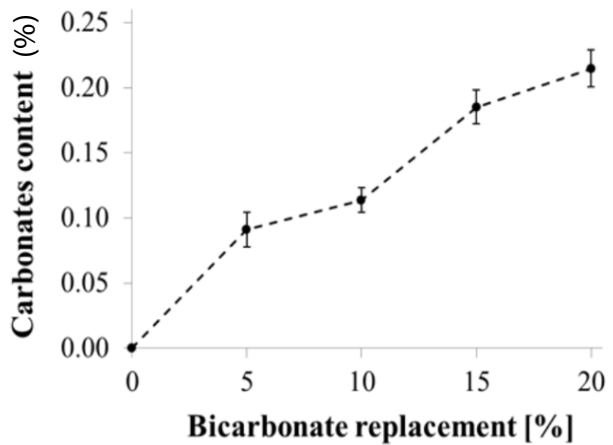


Figure 5. As the percentage of bicarbonate replacement increases, the amount of carbonates in the sample increases, shown quantitatively in Figure 4 as the area-fraction of carbonate groups in the Raman maps.

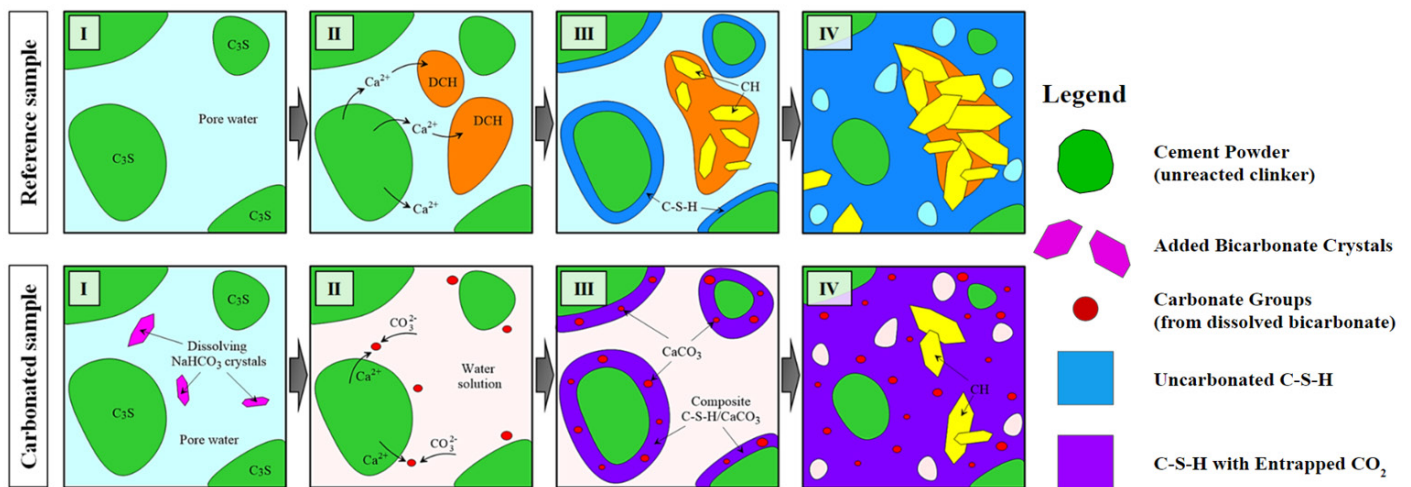


Figure 6. A schematic representation of early-stage hydration reactions for samples with and without bicarbonate addition. In reference sample, the binder C-S-H has no embedded carbonates after curing. In carbonated concrete, however, carbonates from sodium bicarbonate crystals accelerate the formation of C-S-H around particles of clinker, trapping  $\text{CO}_2$  (in the form of carbonates) in the material.

# Roadmap to Early-stage Carbonation

These results suggest that early-stage pre-cure carbonation is a pathway for concrete to store a controlled and precise quantity of CO<sub>2</sub>. It is possible that the theoretical CO<sub>2</sub> uptake capacity of concrete due to early-stage carbonation can be sufficient to offset **at least 40% of the calcination emissions associated with cement production** [6]. This assumes that there is no CO<sub>2</sub> associated with the production of sodium bicarbonate; our work anticipates advances in the lower-emissions production of sodium bicarbonate [8, 9]. At the level of sodium bicarbonate substitution analyzed, not all CH was consumed, minimizing adverse effects on pH levels. Evaluating long term effects on pH levels is a priority for our future work.

CIPCC offers a further example of why government and industry stakeholders must consider the potential life cycle savings and impacts of carbonation. The increase in early stage strength shown in Figure 2 could speed up construction by allowing concrete to reach its full strength more quickly in real world applications. **With this objective in mind, future CSHub work will aim to push the limits of carbonated concrete in industry-applicable OPC models using various bicarbonates, and to quantify the material's CO<sub>2</sub> uptake through life cycle assessments.**

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## Endnotes

- [a] In concrete that is reinforced with steel, the corrosion process can be initiated if the carbonation happens extensively (e.g., the whole of the concrete cover is carbonated) and intensively (e.g., a significant proportion of the hardened cement product is carbonated). We define concrete cover as the layer distance between the surface of reinforcement and the outer surface of the concrete.
- [b] Former CSHub researcher Hyun-Chae Loh observed disordered calcium hydroxide (DCH), an amorphous phase that forms in concrete before the material sets, which was previously unobserved in laboratory conditions [5]. Raman microscopy revealed that during CIPCC, DCH carbonates to form another transient phase called disordered calcium carbonate (DCC), which can be found alongside other polymorphs of calcium carbonate in calcium silicate hydrate (C-S-H).
- [c] Thermogravimetric analysis (TGA) allows for a sample's contents to be quantified by mass. Full TGA results can be viewed in the published PNAS Nexus paper [6].

## Related Links:

- [MIT CSHub, "C-S-H: Water, Water Everywhere](#)

## Citation:

Hajduczek, M., and Stefaniuk, D. (2023). Carbonation Before Curing: A New Path to Concrete Sustainability. *Research Brief*. Volume 2023, Issue 2.

This research was carried out by MIT CSHub, which is sponsored by the Concrete Advancement Foundation. CSHub is solely responsible for content.