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Enzymatic Carbon Sequestration in Cementitious Materials

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ABSTRACT

Concrete can act as a carbon sink since CO₂ penetrates and reacts with Ca(OH)₂ in concrete resulting in the carbonation of concrete, which is a natural process. However, this process is slow due to different factors. Carbonic anhydrase (CA) is a group of enzymes that could be a promising candidate to accelerate CO₂ sequestration. CA acts as a catalyzer for CO₂ hydration to H⁺ and HCO₃⁻ and has been reported to increase the reaction rate by about 10⁷ times compared to the process in the absence of CA. Larger amounts of CO₂ may thus be sequestered via carbonation in a shorter period. We aim to achieve efficient atmospheric CO₂ sequestration in cementitious materials with the help of CA. Preliminary results show that CA maintains enzyme activity and accelerates CO₂ hydration in alkaline solutions representative for concrete. Cement pastes with trace amounts of CA exhibited higher carbonation rate at the early stage compared to CA-free cement pastes. While these results are encouraging, more research is needed for further understanding the mechanisms of CA carbonation acceleration in concrete.

KEYWORDS: *CO₂ Sequestration, Carbonic Anhydrase, Cementitious Materials*

1. Introduction

The emission of CO₂ has increased rapidly in the last decades which has pushed the global environment out of safe boundaries. Research has focused on different technologies for reducing atmospheric CO₂, such as geological sequestration, chemical absorption, physical separation, membrane separation and biological fixation (Stewart & Hessami 2005). Nowadays, the biological sequestration technique has attracted many types of research to mitigate the influence of excessive CO₂ because of its low cost and eco-friendliness compared to widely used geological and chemical techniques (Arora 2018).

Bio-sequestration is usually achieved by living organisms, such as bacteria and fungi, via Microbially Induced Calcite Precipitation (MICP) process. MICP is a widespread biochemical process with the formation of CaCO₃ crystals in nature all around the world. MICP is the result of interactions between metabolic activities with organic and inorganic compounds present in the surrounding environment. The major metabolic processes involved in MICP include urea hydrolysis, photosynthesis, denitrification, dissimilatory sulphate reduction, nitrate reduction (Song, et al. 2022). However, the chemical environment around the living organisms may negatively affect MICP, such as high pH, low water content, and limited energy source. All living organisms require appropriate living conditions to maintain the metabolic activities for MICP. In addition, the heterotrophic living organisms are not able to use the atmospheric CO₂ directly, instead they produce CO₂ during the respiration.

A very important enzyme produced by living organisms is involved in MICP, namely carbonic anhydrase (CA), which can accelerate CO₂ hydration dramatically compared to that of process in the absence of CA. CA is an enzyme containing Zn²⁺ in its active site, and it catalyzes the reversible reaction of CO₂ and H₂O (Eq. 1) (Shekh, et al. 2012).



The charges on Zn^{2+} attract the oxygen of H_2O and the binding of H_2O to Zn^{2+} lowers the pKa of H_2O , promoting the removal of H^+ and leaving OH^- bound to Zn^{2+} . The CO_2 hydration is initiated by the nucleophilic attack of zinc-bound OH^- , generating zinc-bound HCO_3^- . The active sites are regenerated by replacing HCO_3^- with H_2O and the catalysis cycle continues (Shekh, et al. 2012). The unique catalytic properties of CA lead to the acceleration of CO_2 sequestration by accelerating hydration of CO_2 and release HCO_3^- up to 10^7 time faster than the CO_2 hydration process in the absence of CA (Bond, et al. 2001).

Concrete can act as a carbon sink since CO_2 penetrates concrete and reacts with cement hydration products to produce $CaCO_3$ in the presence of water. Nevertheless, the rate of natural carbonation process in concrete is limited due to different factors, such as CO_2 concentration in the atmosphere, water content in the concrete, and concrete porosity. Our hypothesis is that CA may be applied for accelerating the carbonation process in concrete due to the excellent catalysis efficiency. In this study, the performance of CA enzyme for CO_2 sequestration in cementitious materials was investigated.

2. Materials and Methods

2.1 Solution pH Measurements

To study the CA activity in the high pH environment, the pH of NaOH solution with different CA concentrations was monitored upon exposure to air. A higher pH decrease rate suggests a higher CA activity. 10 mL of 6 mM NaOH solutions contained 0, 1.2, 2.4 μM CA (from Sigma-Aldrich), respectively, were prepared for pH measurements. The pH sensor was placed in solution at given intervals to monitor the pH changes.

2.2 Cement Pastes Preparation

A CA solution with a concentration of 20 μM was prepared by dissolving the CA enzyme powder into deionized water. CEM I 42.5 N cement from Holcim was used to prepare cement paste with a water-to-cement ratio of 0.4. 200 g of cement was mixed in a mixer at a low speed (approximately 140 RPM) for 30 s, and then 80 g of water containing 1 ml of the 20 μM CA solution was slowly added while the mixer continued at the low speed for 60 s. After checking that no dry materials settled at the bottom, the mixing continued for 60 s at the speed of about 580 RPM. The thoroughly mixed materials were cast in plastic bottles with diameter of 31 mm and sealed for curing. The control samples without CA were prepared in the same way but without adding CA powder into water. The plastic bottles were removed after curing for 17 days and the cement pastes were cut into slices with 2 mm thickness. The slices were divided into three groups and exposed to different environments, namely, 20% CO_2 , natural carbonation (ambient environment), and sealed in plastic containers, respectively. The slices were crushed and sieved to select particle sizes in range of 0.6 - 1.2 mm for further analyses after 3, 7, and 14 days, respectively.

2.3 Thermogravimetric Analysis (TGA)

TGA tests were performed with Q50 TGA (TA instruments) under the purge flow of nitrogen gas with a rate of 20 mL/min. About 50 mg cement paste were collected for each measurement, and the measurement was performed following the program of (1) heating from room temperature to 105 °C with the rate of 10 °C/min, (2) holding for 30 min, and (3) heating from 105 °C to 1000 °C with the rate of 10 °C/min (Zhang & Scherer 2020).

3. Results

3.1 Solution pH

CA catalyzes the hydration of CO_2 , and consequently, H^+ ions from the reactions are released to the surrounding solution resulting in a pH decrease. Therefore, measuring pH is a viable method to monitor the progress of this enzymatic reaction (Mirjafari, et al. 2007). The results are shown in Figure 1. Faster pH

decrease was achieved with higher CA concentration. The results show that the CA enzyme is active at high pH environment and can effectively accelerate CO₂ hydration.

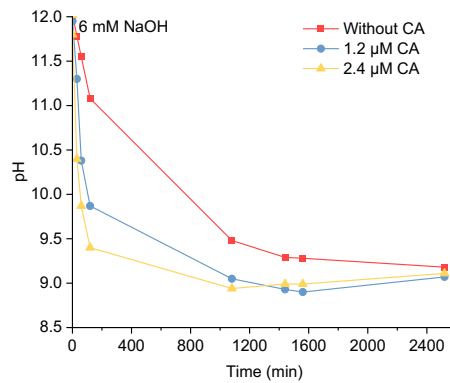


Figure 1. pH of 6 mM NaOH solution with 0, 1.2, 2.4 μM CA, respectively.

3.2 Thermogravimetric Analysis (TGA)

The weight losses curves can be obtained from TGA tests. Figure 2a) shows that samples exposed to 20% CO₂ exhibited the highest weight losses, which is due to the most thermal decomposition of the carbonate phases. The natural carbonation groups showed slightly higher weight losses than that of sealed groups. Several peaks can be identified due to decomposition of different phases from the derivative weight losses curves in Figure 2b). First peak between 105 and 200 °C is due to the release of water from C-S-H and/or the decomposition of small amounts of ettringite (Hall, et al. 1996). The peaks at around 450 °C referring to the decomposition of CH, which is one of the main hydration products of cement. The sealed and natural carbonation groups display higher CH peaks than that of samples exposed to 20% CO₂ since more CH was carbonated to CaCO₃ for higher CO₂ concentration. The following larger peaks in higher temperature range can be assigned to the decomposition of CaCO₃. The samples exposed to 20% CO₂ exhibit multi-peaks at the range of 550 to 750 °C. The peaks at lower temperature are believed to be metastable CaCO₃, such as vaterite and aragonite, and peaks at higher temperature are due to calcite, which has the highest thermodynamic stability among the polymorphs (Radha, et al. 2010).

The temperature range of different peaks were identified individually for each derivative curve. The amount of CaCO₃ shown in Figure 2c) was calculated from the derivative curves. For the samples exposed to 20% CO₂, CA enzyme acts as a booster for carbonation and more CaCO₃ was obtained during the first week, while after one week the samples without CA exhibited the same amounts of CaCO₃, indicating the CA effect might be suppressed. The explanation for this “catch-up” could be that samples with CA enhanced carbonation process and reached the maximum carbonation faster than these without CA. Another hypothesis is that further carbonation became difficult after 1 week at 20% CO₂, possibly due to microstructural changes. For instance, the precipitation of CaCO₃ may form shells on CH crystals so that HCO₃⁻ (and CO₃²⁻) ions cannot easily reach the interior of CH crystals for further reaction. Another reason could be that the pores in the surface layer of cement paste were blocked with CaCO₃, hindering CO₂ ingress into deeper layer. The samples exposed to natural carbonation conditions exhibited much lower CaCO₃ formation, which can be explained by the CO₂ concentration that was 500 times lower than for the series exposed to 20% CO₂.

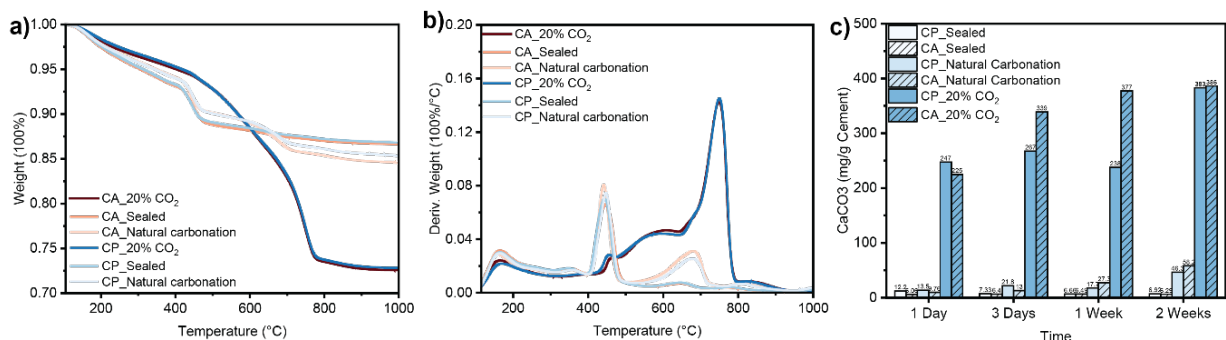


Figure 2. a) TGA weight loss curves for cement paste with and without CA, and b) derivative weight loss curves with and without CA (Only curves of samples in different environment after 14 days are shown). c) the calculated CaCO₃ amount in cement pastes. CP refers to cement paste without CA enzyme and CA refers to cement paste with CA enzyme.

4. Conclusions

The catalytic ability of CA suggests a promising potential for CO₂ sequestration applications in cementitious materials. In this study, we evaluated the CA enzyme activity under high pH conditions and quantified the CO₂ sequestration capacity of the enzymatically modified cement pastes. The pH measurements results indicated that CA could maintain the enzyme activity in high alkaline conditions and CA can effectively accelerate the CO₂ hydration. Higher CO₂ hydration process could be achieved with a higher CA concentration. In cement pastes, CA could accelerate carbonation process at the early stage, then the carbonation was retarded probably due to the microstructural changes. Further experiments will be conducted to investigate porosity, pore structures, and other microstructure properties in order to further understanding the interactions between CA and the cement paste. Although the CA enzyme does not affect the ultimate CO₂ sequestration capacity of materials, it can significantly accelerate the process of CO₂ sequestration in cementitious materials. As a result, a substantially greater amount of CO₂ can be sequestered within the same time period when CA is present compared to when it is absent.

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