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# Microwave-based Preconditioning Technique for Accelerated Carbonation Curing of Cementitious Materials

Min Liu[a], Neil Milestone[a,b], Yun Bai[a*]
[a] Department of Civil, Environmental and Geomatic Engineering, University College London, London, UK
[b] Milestone and Associates, New Zealand.

## ABSTRACT

Carbonation curing is being considered as an alternative method to replace steam curing. Not only is early strength enhanced quickly but $CO_2$ is absorbed as well. However, the water/cement ratio suitable for carbonation curing is very low, far below than that used in mixing. In this paper, microwave heating is proposed as an alternative preconditioning method to facilitate carbonation curing, with the whole process lasting only 4 hours.

Our aim is to show the potential of using microwave heating as a preconditioning method prior to carbonation. The effectiveness of both sealed microwave and water bath heating as an alternative preconditioning method for carbonation curing is shown by strength gain results and carbonation uptake, with the results to be similar. Quantitative X-ray diffraction (QXRD) was used to determine the carbonation products and the consumption of calcium silicates. The majority of the carbonation products were calcite, with a very high consumption of calcium silicates shown after carbonation. Scanning electron microscopy (SEM) was carried out to follow the microstructural changes. The results obtained suggest a new preconditioning method prior to carbonation curing which is highly efficient, and enables a wider application of concrete with a lower aggregate/cement ratio and vibration during the moulding.

## 1. INTRODUCTION

In carbonation curing, cementitious materials are placed in a $CO_2$ atmosphere at an early age, usually within 24 hours of casting. This curing method enhances early strength quickly and as well, absorbs $CO_2$ [1]. Studies also suggest this method could enhance durability and improve long-term performance of concrete [2].

The mechanism behind carbonation curing lies in the fact that $CO_2$ quickly reacts with calcium silicates to form C-S-H gel and $CaCO_3$, as well as reacts with the hydrated products, such as $Ca(OH)_2$ and the high calcium/silicate ratio C-S-H gel to form $CaCO_3$ and C-S-H gel with a lower calcium/silicate ratio. The equations are shown below [3].

$$C_3S + (3-x)CO_2 + yH_2O \rightarrow xCaO.SiO_2.yH_2O + (3-x)CaCO_3 \quad (1)$$

$$C_2S + (2-x)CO_2 + yH_2O \rightarrow xCaO.SiO_2.yH_2O + (2-x)CaCO_3 \quad (2)$$

$$C_xSH_y + CO_2 \rightarrow C_{x'}SH_{y'} + CaCO_3 + H_2O; x > x', y > y' \quad (3)$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \quad (4)$$

The increased amount of C-S-H gel formed helps enhance the early strength and reduces porosity. In the meantime, conversion of $Ca(OH)_2$ to $CaCO_3$ also helps decrease porosity. Both effects result in a lower permeability and enhanced strength.

Despite these advantages, there are issues that restrict the application of carbonation curing. The carbonation process requires $CO_2$ to intimately contact the cementitious materials. However, normally a water/cement ratio of no less than 0.4 is required by mortar or concrete to guarantee sufficient workability, and this water content is too high for a carbonation curing process. The layer of water on the surface of cementitious particles can stop the $CO_2$ from diffusing to the interior and prevents it from reacting with the cementitious materials.

Preconditioning methods prior to carbonation are proposed to solve this problem. These include exposure to lower humidity for several hours or the application of fan drying [4] [5]. However, this takes a relatively long time and weaken the advantage of carbonation curing in developing a high early strength.

Microwave heating, where electromagnetic energy is applied, is identified as a potential alternative preconditioning method. Microwave

energy heats the samples homogeneously, making it much more efficient for curing cementitious materials compared with steam curing. It even requires no delay time and has a much higher rate of temperature increase [6] [7]. Despite the evaporation of water from heating, the heating itself could also be able to combine evaporable water, making the whole preconditioning process more efficient. In addition, a unique 'pumping effect' – where the air bubbles exposed to direct heating inside specimens could expand and make paths for extra evaporation, leading to a higher efficiency of carbonation [8].

The purpose of this paper is to investigate if microwave heating can serve as a preconditioning method to facilitate carbonation curing. The comparison with water bath heating was made to confirm the role that temperature plays. The effects of carbonation were studied through compressive strength, phenolphthalein test and microstructural analysis.

## 2. Materials and experiment

### 2.1 Materials

Portland CEM I 52.5N cement, supplied by Castle Cement Ltd, UK, was used throughout the experiment. The quantities of $C_3S$, $C_2S$, $C_3A$ and $C_4AF$ were 62.2%, 15.8%, 5.8% and 7.4% respectively. Standard sand was used to reduce variations between mixes.

### 2.2 Experiment

Cement, sand and water were mixed at a weight ratio of 1:2:0.4 for 5 minutes, before being vibrated well into moulds. Then the samples were sealed and put in a tailor-designed microwave oven and a water bath for 70 minutes. In the microwave oven, the temperature inside the samples was set to increase to 70 ℃ in 15 minutes and then maintained for 55 minutes. In the water bath, the temperature of water was set at 73 ℃which ensured the temperature profile inside the samples was close to that in the microwave oven. After preconditioning, half of the samples were demoulded and tested for compressive strength, while the rest were put in a pressure vessel, at a $CO_2$ pressure of 5 bar, for 2 hours. The samples were then taken out for strength measurement and the phenolphthalein test.

After the strength test, the broken specimens were crushed to a powder and put in a furnace to measure $CO_2$ uptake. The mass loss between 500 ℃ and 1000 ℃ was considered as the sequestered $CO_2$, with its ratio to cement mass taken as the carbonation uptake.

The top layer of the specimen (12.5 mm) was crushed into small pieces and put in acetone to stop hydration. Some pieces were ground to pass 63 μm sieve for quantitative XRD with corundum as an internal standard, and other pieces were prepared for SEM test.

## 3 Results and discussion

### 3.1 Compressive strength

From Fig. 1, it can be seen that there is a noticeable increase in strength after carbonation. It should be noted that specimens cured under room temperature are still in its plastic stage with no strength being developed. However, following sealed microwave preconditioning, after 2 hours' carbonation, the strength can be as high as 24.6 MPa; with water bath conditioning, strength also reached up to 23.1 MPa. By contrast, the strength before carbonation was very small, with only around 1.5 MPa.

The above results prove that both microwave heating and water bath heating can provide efficient preconditioning, with the former slightly higher. Following preconditioning heating, the strength can be largely improved by carbonation.

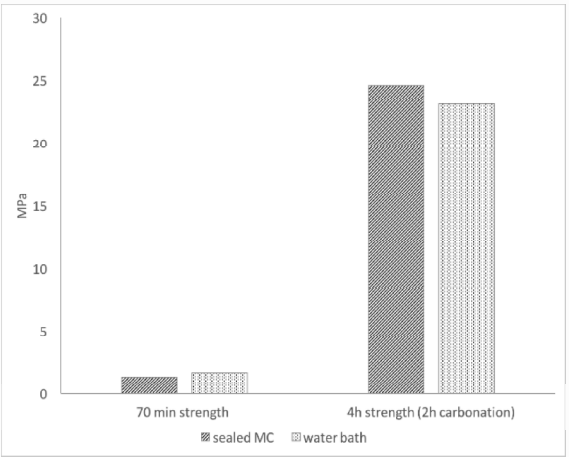


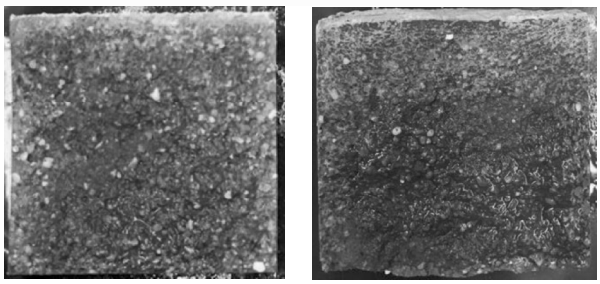

**Figure 1.** Compressive strength before and after carbonation

### 3.2 Phenolphthalein test

The phenolphthalein tests for each specimen are shown in Fig. 2. For both preconditioning methods, the pictures show a similar carbonation depth. In addition, unlike the tests in most references which showed a homogeneous

carbonation on the top and bottom [9], the both specimens in this experiment had more carbonation on the top and less carbonation on the bottom.

This higher carbonation degree on the top than bottom could result from the fact that as the specimens were sealed during heating, more moisture could be lost from the top of specimens, allowing more carbonation to occur on the top of the specimens.



(a) microwaved (b) water bath

**Figure 2:** Carbonation profile

### 3.3 Carbonation uptake

$CO_2$ uptake is an important indicator for the sequestration of $CO_2$ itself. From Table 1, the carbonation uptakes for both preconditioning methods were similar, with the microwave cured sample slightly higher, which is in corroboration with the strength data. The theoretical maximum uptake could be around 50% [10], higher than seen in this experiment. However, as can be seen from phenolphthalein test, it was different for different layers. While it was around 14% for the whole sample, the figure for the top layer could be much higher.

**Table 1.** Carbonation uptake of microwave and water bath preconditioned specimens

| Regime | $CO_2$ Uptake |
|---|---|
| Sealed MC 70 min & carbonation | 14.1 |
| Water bath & carbonation | 13.5 |

The figures for $CO_2$ uptake, strength and phenolphthalein tests all show the efficacy of microwave heating. The carbonation results for microwaving were similar to those for water bath heating, which had a similar temperature profile: this suggests temperature profile is a more important factor. The unique 'pumping effect' [8] does not show any specific advantage which could be due to the relatively low temperature (70 ℃) making it unable to generate enough pathways for evaporation and subsequent carbonation.

### 3.4 XRD results

QXRD results for specimens before and after carbonation are displayed in Fig. 3. It can be seen that the amounts of ettringite (AFt), CH and calcium silicates have been largely reduced after 2 hours' carbonation. CH and AFt still existed in the top layer after carbonation, indicating the samples were not fully carbonated even on the top layer. There were noticeable decrease in the peaks of calcium silicates, showing a high degree of consumption of calcium silicates, which would normally not hydrate far at early stage without carbonation curing. Two types of $CaCO_3$ exist, with calcite the main carbonation product and a small amount of aragonite.

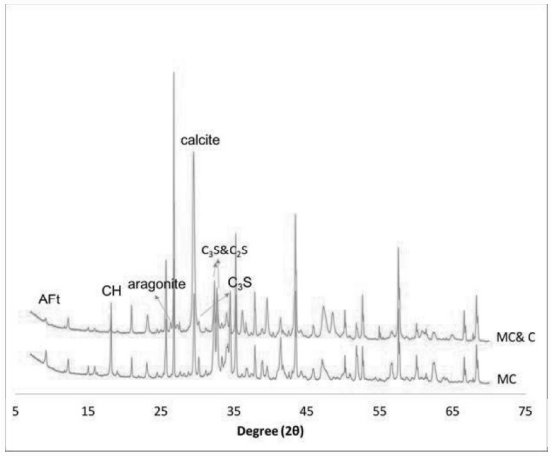



**Figure 3.** XRD traces of microwave preconditioned samples before and after carbonation

Table 2 shows the specific change of the amount of calcium silicates and calcite. The amount of calcium silicates in the raw materials were 78%, while this figure dropped to 39.9% after 30 minutes delay and 70 minutes microwave heating. While the hydration could be rapid at early times, this should slow down as hydration proceeds further [11]. However, after carbonation, the $CO_2$ consumption was very high, and the retained calcium silicates reduced to only 13%. In the meantime, the amount of calcite increased from 2.13% to 28%, showing most carbonation products were calcite.

**Table 2.** Amount of calcium silicates and calcite before and after carbonation

| | $C_3S + C_2S$ (%) | Calcite (%) |
|---|---|---|
| MC only | 39.9 | 2.13 |
| MC & carbonation | 13 | 28 |

This again demonstrates the rapid consumption of calcium silicates. As a consequence, more C-S-H gel would be created, accompanied by a higher amount of $CaCO_3$. Both carbonation products would contribute to the compressive strength of carbonated products.

3.5 SEM results

Fig. 4 shows the microstructure of microwave preconditioned specimens before and after carbonation. Before carbonation, there was noticeable C-S-H gel on the surface of particles which corroborates well with the calcium silicates consumed in Table 2. However, no obvious C-S-H gel was present after carbonation, but instead, a layer of carbonation products showed on the surface of cement particles. The SEM images showed that the cement particles were coated with a surface layer of calcite, which could prevent it from further carbonation.

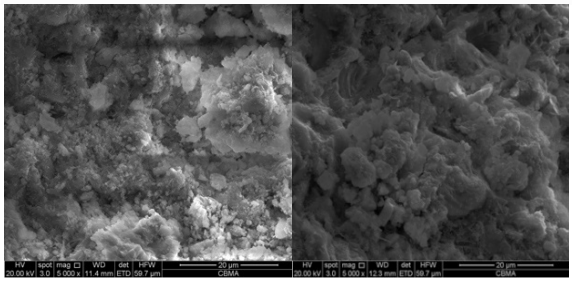


**Figure 4.** SEM images of carbonated and uncarbonated specimens at 4 h
(a) sealed MC (x5000) (b) sealed MC & carbonation (x5000)

## 4 Conclusion

Based on the above discussion, the following conclusions can be drawn.

1 Microwave heating could serve as an efficient preconditioning method for carbonation curing, shown by largely improved 4 h strength as well as large carbonation uptake.
2 A similar temperature profile, from either microwave heating or water bath heating, contributes to comparable strength and carbonation uptake.
3 There is a significant consumption of calcium silicates after carbonation.
4 While obvious C-S-H gel after heating is shown from SEM image, this was not obvious after carbonation. Instead, a layer of calcite formed on the surface of cement particles after carbonation curing.

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