

Evaluation of Carbonation Degree of Hardened Cement Paste with Different Water-Cement Ratio in Wet-Dry Cycle

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Abstract. *One of the global environmental problems, CO₂ emissions from cement production intensifies in these decades. To solve this problem, countermeasures for CO₂ emissions using waste concrete, which has ability to absorb CO₂ due to contain calcium-silicate-hydrate (C-S-H) and portlandite (Ca(OH)₂), are in the spotlight recently. However, considering the limited time before recycling as roadbed materials, it is important to increase CO₂ absorption efficiency so that as much CO₂ as possible reacts with waste concrete. In this study, hardened cement paste powders (HCPWs) with the water-to-cement ratios of 0.4, 0.5 and 0.6 were evaluated for the degree of carbonation under various humidity conditions. HCPWs were pulverized to a particle size of 0.6 to 1.18mm and put in desiccators keeping constant humidity condition of RH60 and RH80. In addition, desiccators were prepared with RH60-80 cycle (wet-dry cycle) of 30 minutes, 1 hour, 2 hours and 4 hours to determine the degree of carbonation promotion according to periodic humidity changes. The degree of carbonation of HCPWs were measured by thermogravimetric analysis (TGA). The result shows that the degree of carbonation was improved as the water-cement ratio increased, because the higher the water-to-cement ratio, the more open pores were contained. In addition, vaterite and aragonite caused by the decomposition of C-S-H were the most produced under RH60-80 cycle conditions. This is considered to be because the reaction area with CO₂ was increased by weakening the C-S-H by repeating drying and wetting.*

Keywords: *CO₂ absorption, carbonation, waste concrete, hardened cement paste powder, wet-dry cycle*

1. Introduction

Global warming has intensified in recent years with the increasing release of large amounts of CO₂ from cement production. Many methods have been proposed to combat this problem, such as using CO₂ to cure concrete and the use of waste concrete containing calcium silicate hydrate (C-S-H) and portlandite (Ca(OH)₂) to absorb CO₂. However, it takes much time and space for waste concrete to store and absorb CO₂. Due to these limitations, improving absorption efficiency becomes an important part of this method. It is known that many factors like water-to-cement ratio, relative humidity, temperature, CO₂ concentration, and particle size can influence concrete carbonation. High water-to-cement ratio leads to more cement hydration and capillary pores content, promoting carbonation and CO₂ absorption (Mehdizadeh et al. 2021). Moreover, relative humidity has an important role in CO₂

absorption. Carbonation is inhibited due to water scarcity under low RH conditions; however, a higher RH also restricts carbonation by preventing the diffusion of CO₂. Meanwhile, According to Zajac et al. 2022, at RH values below 80%, the degree of carbonation is low and nearly independent of RH for 50% < RH < 80% whereas the amount of CaCO₃ increases at higher RH significantly targeting particle size than 100µm. Therefore, this study analyzed the aspects of different water-to-cement ratios on the degree of carbonation. The humidity environment suitable for carbonation of hardened cement paste was also studied.

2. Materials and Methods

2.1 Materials

In this study, hardened cement pastes with three different water-to-cement ratios of 0.4, 0.5, and 0.6 were produced using ordinary portland cement. These samples were sealed curing for more than 28 days at 20°C. Then these hardened cement pastes were pulverized by a ball mill to a size of 0.6 to 1.18 mm to mimic the actual sizes of by-product of waste concrete.

2.2 Methods

2.2.1 Experiment conditions

Three kinds of hardened cement paste powders (HCPWs) with water-to-cement ratios of 0.4, 0.5 and 0.6 were put in every desiccator with different humidity condition of RH60, RH80, and the cycle RH60-80 of 30 minutes, 1 hour, 2 hours, and 4 hours. The temperature and the CO₂ concentration in desiccators were 20°C and 0.03%, respectively. The experiment conditions are shown in Table 1.

Table 1. Experiment conditions.

Relative humidity	RH 60	RH 80	RH 60-80
Cycles	-	-	0.5 h, 1 h, 2 h, 4 h
Temperature and CO ₂ concentration	20°C, 0.03% (concentration in the atmosphere)		
Water to cement ratio	0.4, 0.5, 0.6		
Particle size of HCPW	0.6 ~ 1.18 mm		
Periods	3 days, 7 days, 14 days		

2.2.2 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is to measure the mass of a substance as a function of temperature or time at a programmed controlled temperature so that analyze the information about the composition, thermal stability, thermal decomposition and so on. In this study, After 3 days, 7 days, and 14 days of carbonation in the desiccators with different humidity

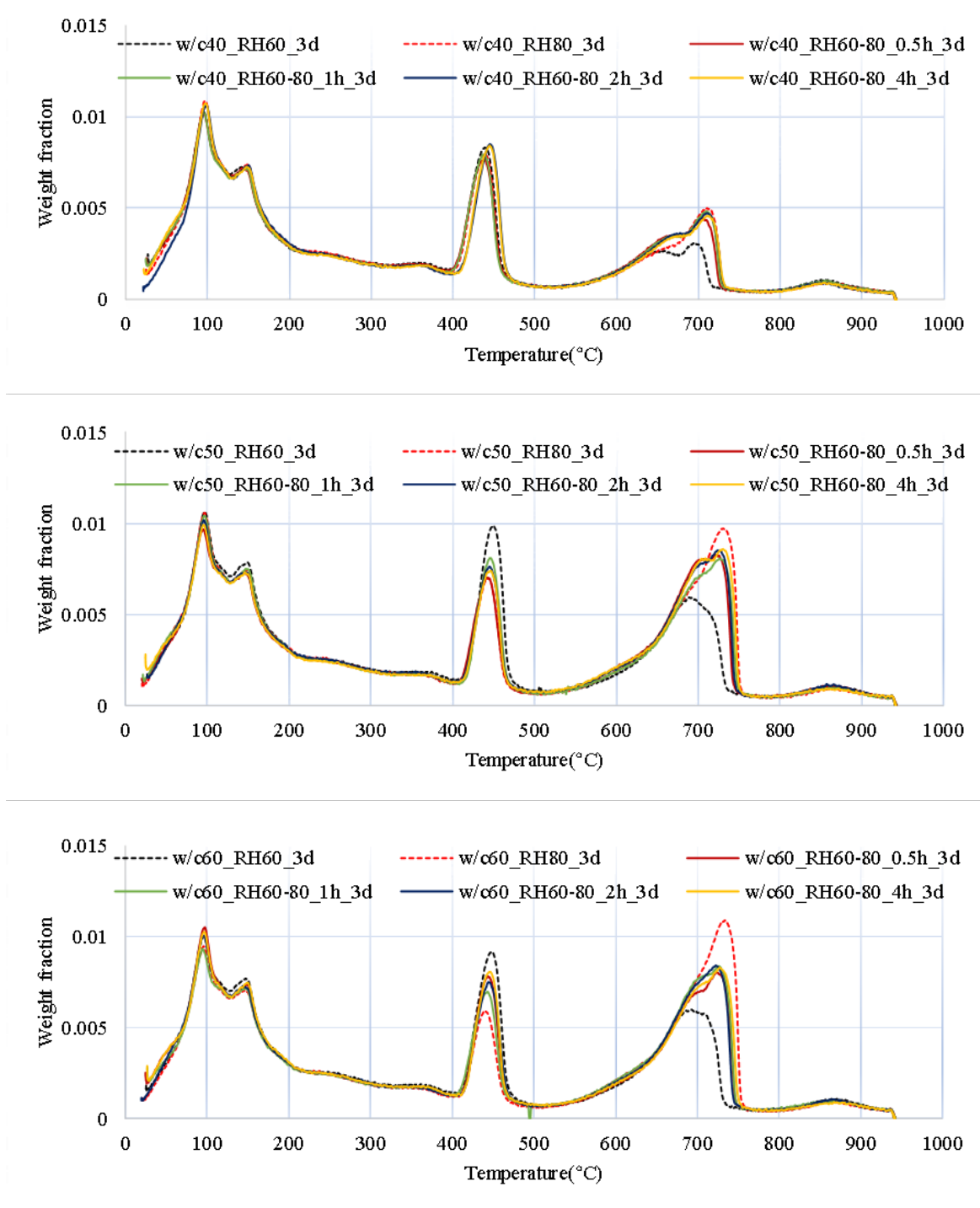
conditions, carbonated HCPWs need to be dried in vacuum desiccators with a temperature of 30°C more than 1 day, then the amount of CO₂ absorbed and the ratio of Ca(OH)₂ can be measured by TGA. Measurements were carried out under an N₂ atmosphere. The TGA had a measurement temperature range of 20°C to 950°C with a heating rate of 10°C/min and held for one hour at 950°C.

3. Result and Discussion

Referring to Zajac et al. 2022, amorphous calcium carbonate (ACC) or poorly crystalline CaCO₃ decomposed at 500~650°C, aragonite and vaterite at 650~720°C, calcite at 720~770°C. And according to Liu et al. 2022, the thermal decomposition temperature of C-S-H was between 30°C and 900°C. From the results in Figure 1 (a)-(c), the least amount of calcite was produced under RH60 regardless of w/c ratios. On the 3 days, though RH80 produced the most calcite, the result was very similar to those at wet-dry cycles for the w/c ratio of 0.4. However, when w/c ratios were 0.5 and 0.6, the order of calcite production was RH80, RH60-80, and RH60. Compared with the calcite production for the w/c ratio of 0.5, it was more produced for the w/c ratio of 0.6. This meant that in the early stage, the w/c ratio had significant effects on the RH80 environment, and calcite increased the most by increasing the w/c ratio. Additionally, in RH80, there was no other form of CaCO₃ produced except for calcite. On the 7 days, the effects of the wet-dry cycle were gradually becoming apparent. In RH60-80 (cycle: 1h) calcite produced the most for the w/c ratio of 0.4 and 0.6. And for the w/c ratio of 0.5, calcite produced the most in RH60-80 (cycle: 2h). Meanwhile, amorphous calcium carbonate (ACC) or poorly crystalline CaCO₃ was absent in RH 60 and RH 80, while they were formed under wet-dry cycles for the w/c ratio of 0.5 and 0.6, and the most production was observed under the w/c ratio of 0.5. Therefore, at this stage, it can be seen that ACC or poorly crystalline CaCO₃ was produced due to wet-dry cycles by increasing the w/c ratio, and it also promoted the production of calcite. And for the w/c ratio of 0.5, all kinds of CaCO₃ were produced most which mean it was more efficient for carbonation. On the 14 days, almost no ACC or poorly crystalline CaCO₃ was produced for the w/c ratio of 0.4, but calcite was produced the most in the wet-dry cycle samples. In contrast, for the w/c ratio of 0.5 and 0.6, ACC or poorly crystalline CaCO₃, aragonite and vaterite also appeared in RH60 as well as wet-dry cycles. According to Zajac et al. 2022, with decreasing water content in the semi-dry process, the content of ACC, vaterite and aragonite increase, whereas the content of the thermodynamically stable phase, calcite, decreases. In addition, the calcite production was almost the same for the w/c ratio of 0.6 except for in RH60. And the carbonation efficiency was still the highest for the w/c ratio of 0.5.

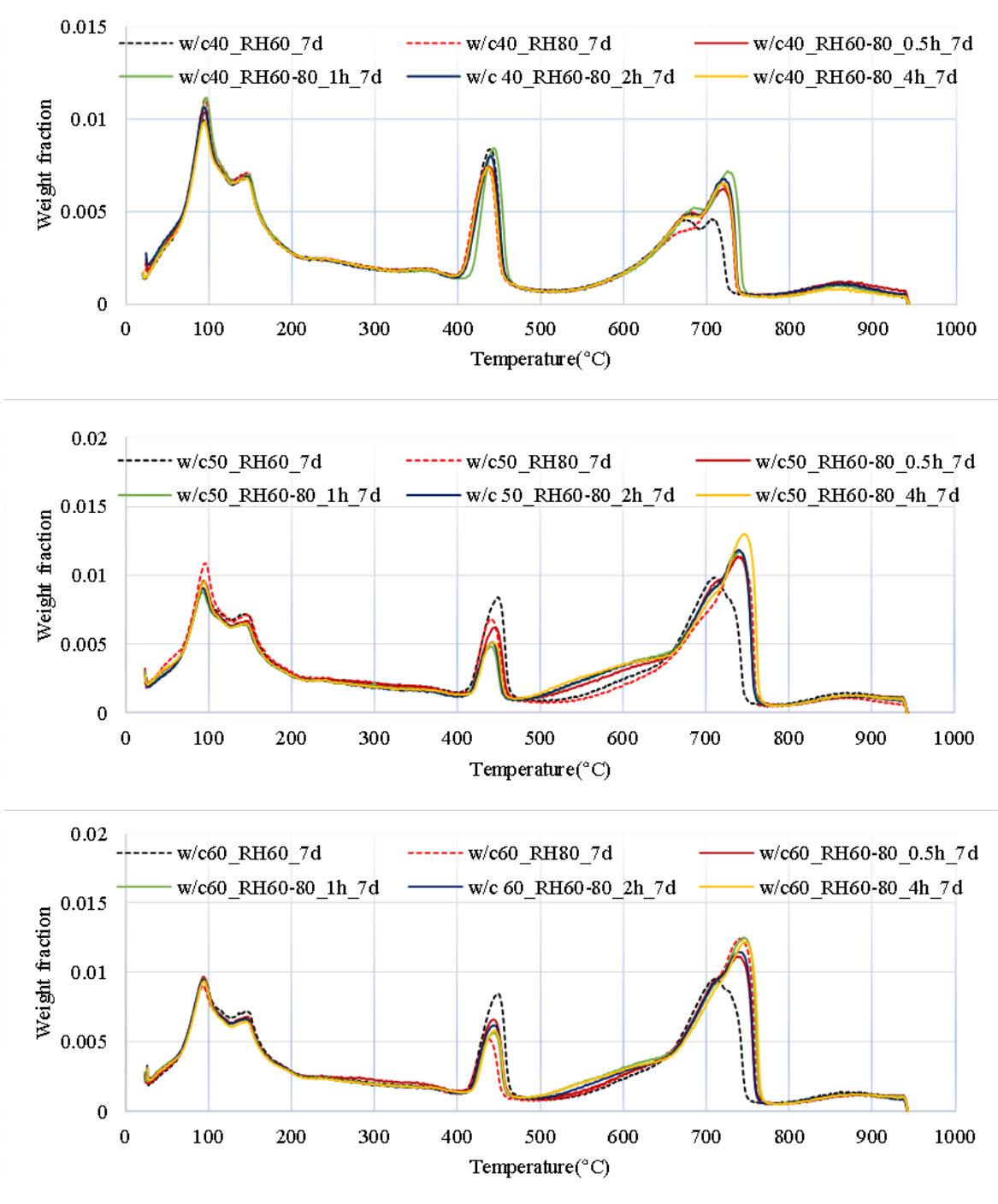
The proportion of Ca(OH)₂ in the carbonated cement pastes and CO₂ absorption rate by period are shown in Figure 2(a)-(c). On the 3 days, the proportion of Ca(OH)₂ in RH80 was basically the same as RH60-80 for the w/c ratios of 0.4 and 0.5. And for the w/c ratio of 0.6, Ca(OH)₂ was consumed in the order of RH60, RH60-80, and RH80. In the early stage, the more decreased Ca(OH)₂ proportion, the more increased the CO₂ absorption rate for the three different w/c ratios. On the 7 days, for the w/c ratio of 0.4, the proportion of Ca(OH)₂ decreased slightly compared with that on the 3 days and was almost the same as RH80 and RH60-80. But the result of CO₂ absorption on the 7 days, CO₂ was absorbed by wet-dry cycles more than in RH80. It means more C-S-H decomposed under wet-dry cycle condition.

Referring to Martín-Garrido et al. 2021, the uptake of atmospheric CO₂ produces C-S-H gel decalcification and carbonation takes place, and ACC or poorly crystalline CaCO₃, aragonite and vaterite could be produced. RH60-80 (cycle: 1h, 2h, 4h) had the least amount of Ca(OH)₂



(a) 3 days

Figure 1. The results of TGA



(b) 7 days

Figure 1. The results of TGA (continued)

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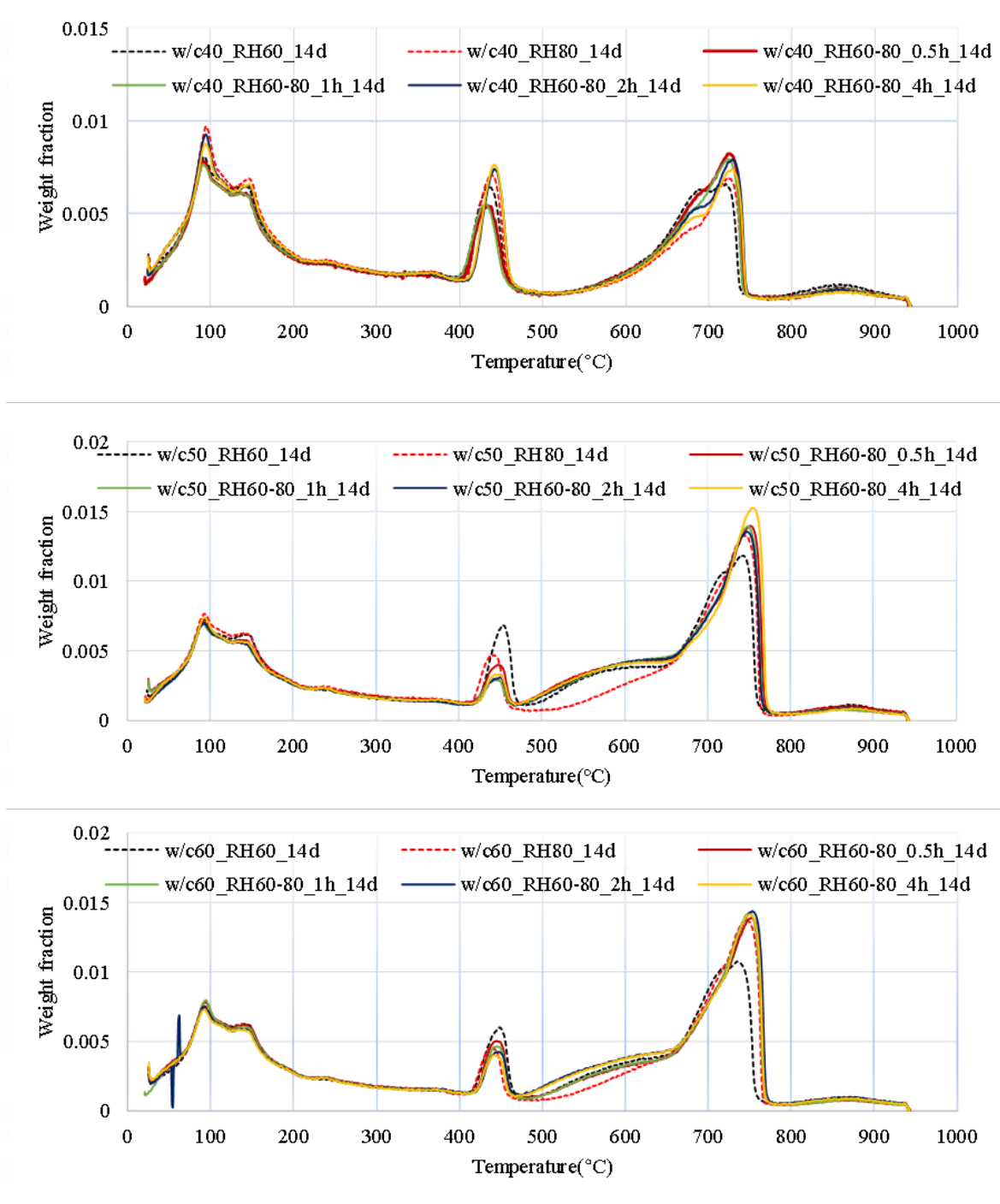
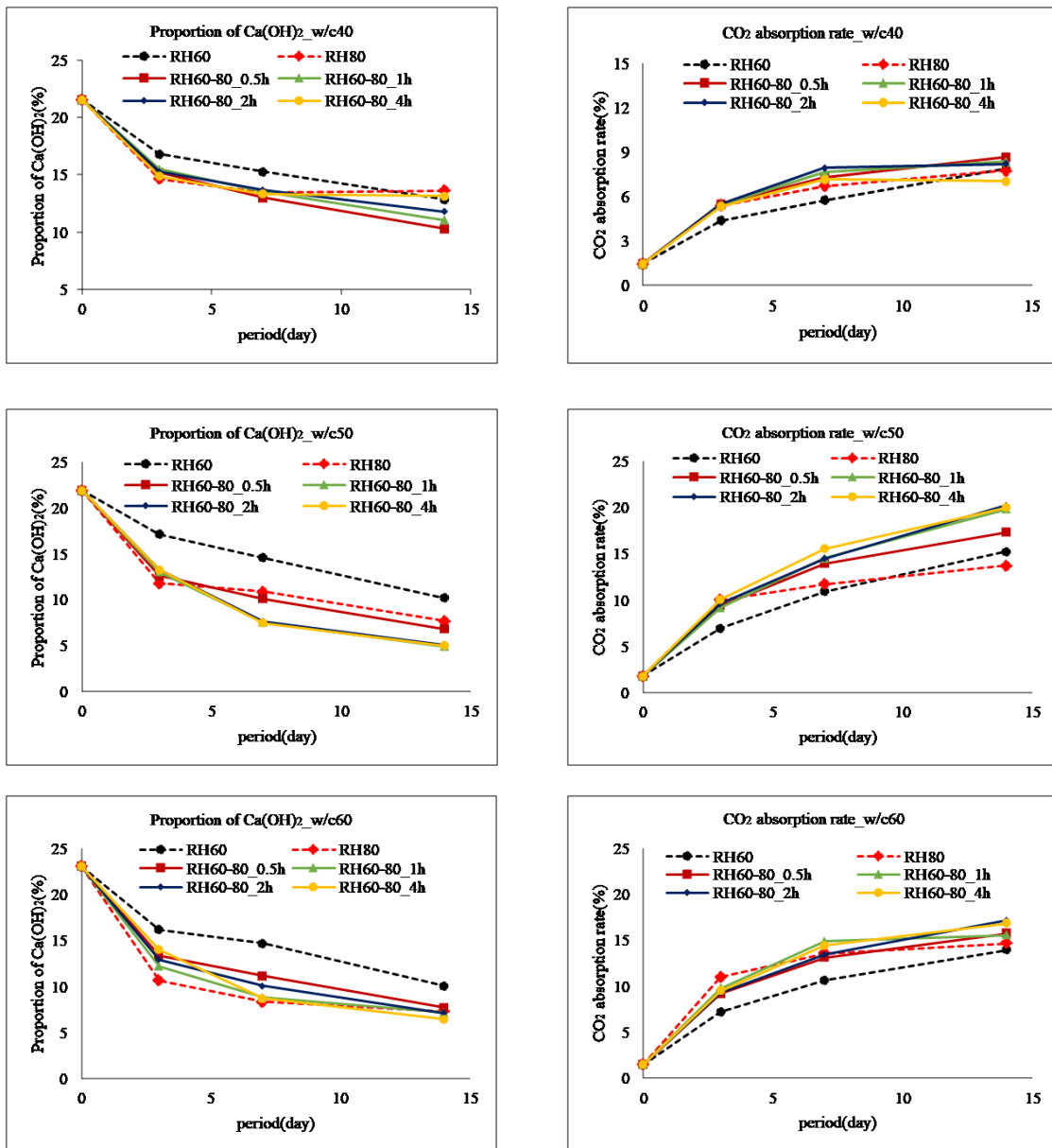


Fig 1. The results of TGA.

for the w/c ratio of 0.5. And the Ca(OH)_2 proportion in RH80 was similar to that in RH60-80 (cycle: 0.5h). However, in RH60-80 (cycle: 0.5h), the CO_2 absorption rate was higher than 20% of that in RH80. It can be seen in RH60-80, ACC or poorly crystallized CaCO_3 ,

aragonite, and vaterite are present due to decomposing the C-S-H. For the w/c ratio of 0.6, the rate of $\text{Ca}(\text{OH})_2$ in RH80 was the same as that in RH60-80 (cycle: 1h, 4h), and both had the lowest amount. The existence of other forms of CaCO_3 was proved by the result of CO_2 absorption in RH60-80 (cycle: 1h, 4h) was more than that in RH80. On the 14 days, for the w/c ratio of 0.4, the consumption of $\text{Ca}(\text{OH})_2$ in RH60 was larger than that in RH80. The proportion of $\text{Ca}(\text{OH})_2$ was very similar to the situation of 7 days for the w/c ratio of 0.5. For the w/c ratio of 0.6, all samples except for RH60 consumed the same amount of $\text{Ca}(\text{OH})_2$, while the rate of CO_2 absorption in RH60 and RH80 was almost same. It can be seen that the absorption of CO_2 by C-S-H under RH60 on the 14 days.



(a) Proportion of $\text{Ca}(\text{OH})_2$

(b) CO_2 absorption rate

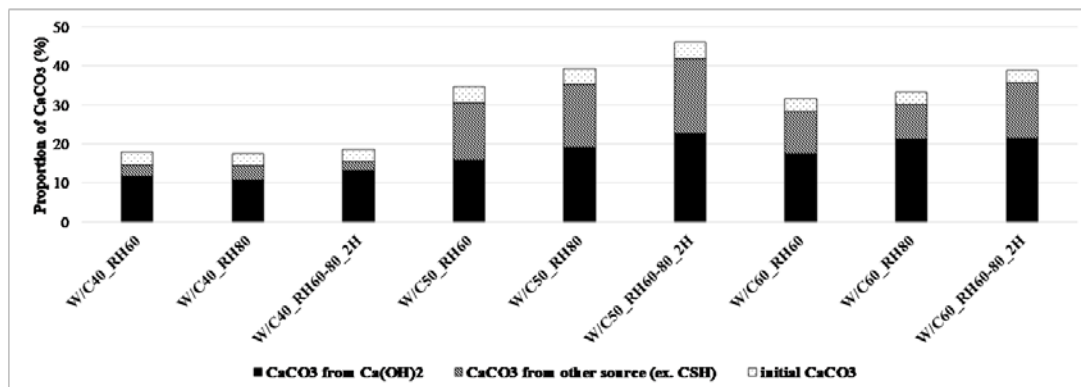
Figure 2. The proportion of $\text{Ca}(\text{OH})_2$ and CO_2 absorption rate of each samples.**Figure 3.** Calcium carbonate production proportion by each source of calcium on the 14 days.

Figure 3 showed the CaCO_3 production proportion by each source of calcium on the 14 days. It was found that the whole production of CaCO_3 was promoted under wet-dry cycle regardless of w/c ratios. And the amount of CaCO_3 was the highest in RH60-80 at w/c ratio of 0.5. Additionally, for the w/c ratio of 0.5 and 0.6, more CaCO_3 generated from C-S-H was found in RH60-80. It was because C-S-H decomposed by repeated wet-dry cycles over time.

4. Conclusions

In this study, TGA was used to analyze the carbonation of HCPWs at different RH conditions of RH60, RH80, RH60-80 (0.5h, 1h, 2h, 4h) and three different w/c ratios of 0.4, 0.5, and 0.6. There were several conclusions as followed:

- As the w/c ratio increases, the size and number of pores within the HCPW become larger, which leads to promoting carbonation.
- RH conditions have an important role in carbonation and being in a wet-dry cycle is more conducive to carbonation. For the low w/c ratio, the effect of RH conditions on carbonation is not significant, while for the high w/c ratio, the C-S-H decomposes due to wet-dry cycles, and aragonite and vaterite are produced on the 7 and 14 days. In addition, for the high w/c ratio, with increasing carbonation time, other forms of calcium carbonate besides calcite were produced in RH60.

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