CORRELATION OF CONCRETE CARBONATION PROCESS UNDER NATURAL CONDITION AND HIGH CO\textsubscript{2} CONCENTRATION ARTIFICIAL ACCELERATED CLIMATE ENVIRONMENTS

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Abstract

Carbonation process of concrete under natural condition and its correlation with high CO\textsubscript{2} concentration artificial accelerated carbonation are of a great concern. The pH values of carbonated concrete were measured, the variation of pH values was determined, and the variations of Ca(OH)\textsubscript{2} and CaCO\textsubscript{3} contents in the carbonated concrete under the natural environment and the high CO\textsubscript{2} concentration accelerated climate environments were determined by microcosmic test methods such as DTA and X-ray diffraction. The experimental results showed that the overall variation trend of pH values and phase component of carbonation layer of concrete under accelerated climate environments with high CO\textsubscript{2} concentrations were the same as those under natural conditions. Therefore, the carbonation processes of concrete were considered consistent under both conditions. However there was a difference in the length of semi-carbonation zones. The one measured under high CO\textsubscript{2} concentration accelerated climate environments was shorter than that under natural condition, which was caused by the differences climate condition (temperature and relative humidity) as well as the properties of the concrete. It is acceptable to simulate the natural condition by applying the high CO\textsubscript{2} concentration artificial accelerated carbonation technique for the purpose of the study of carbonation process of concrete.

1. INTRODUCTION

Corrosion of the steel reinforcement is a serious form of deterioration in reinforced concrete structures. Carbonation itself does not cause the deterioration of concrete, but it changes the pH value of the liquid solution in the pores in concrete. Carbonation is a progressive reaction beginning at the surface of the concrete and penetrating deeper and deeper with time due to the diffusion of carbon dioxide into the concrete. Thus, the
carbonation front within the concrete can be defined as one which advances with time. Traditionally and most simply this front has been identified by spraying phenolphthalein indicator dissolved in alcohol onto a freshly fractured concrete surface [1,2,3], which results in a color change at a pH of approximately 9.5. In reality, the propagation of carbonation is more complex than the results this method suggests, with the degree of carbonation (i.e., the pH change) varying with depth rather than being discrete.

Parrot [4] found the presence of semi-carbonation zone. Researchers afterward defined three zones accordingly, totally carbonated zone, semi-carbonated zone and non-carbonated zone. The principal distinguishing the zones is the corresponding pH values. Non-carbonated concrete has an alkaline pH of approximately 12.6, whereas the totally carbonated concrete is more neutral with a pH value of about 8.3. The pH value in the semi-carbonation zone increases with the depth into the concrete ranging from 8.3 to 12.6, as illustrated in Figure 1 [4].

![Figure 1: pH value profile of carbonation concrete](image)

The length of the carbonation zone and the pH value variation in the semi-carbonation zone are the critical factors that affect the rate of corrosion of the steel. There have been extensive studies in this area of research [5-7]. However, all of them are conducted using accelerated experiments in laboratory with very high CO$_2$ concentrations or pressures. The carbonation process of concrete under natural conditions is rather slow. In the experimental works, it is desirable to accelerate the process to shorten the duration of testing to predict long term performance under natural conditions. It is not clear whether the results obtained under accelerated environment can reflect what is really happening in the natural environment.

The objective of this study is to compare the results obtained under both natural and accelerated environments. First, field tests were conducted. Then the accelerated carbonation experiments were carried out under artificial environment with higher CO$_2$ concentration. The pH value profiles within the samples under both environments were measured. Coupling with DTA and XRD techniques, we will study the correlation between the carbonation processes under atmospheric and artificial environments.
2. EXPERIMENTAL

2.1 Sample preparation

2.1.1 Natural condition

The samples were taken from a column of the housing of a 25 year old boiler in the China University of Mining Technology, Xuzhou, Jiangsu, China. Corrosion cracking was found in the housing concrete structure in 1998, and the facility of the boiler was retired in 2004. The compressed strength of the column was 26.8 MPa. The totally carbonated depth measured by using 1% phenolphthalein indicator was within the range of 20-35 mm. Dust samples were extracted from the surface of concrete inward, corresponding to three totally carbonated locations (24 mm, 27 mm, and 30 mm). Samples were taken every 5 mm in the totally carbonation zones. But samples for the measurement of pH values in the semi-carbonated zones were taken every 2 mm. All the dust samples were stored in a sealed container for measurement of concrete pH values later on in the laboratory.

Samples for XRD/TGA analyses were taken from location with a totally carbonation depth of 28 mm. The coarse aggregate (gravel) was removed leaving only cement mortar. Before the XRD/TGA analyses, the pH values were measured first to determine where exactly this sample was taken from the three zones, totally carbonation zone (10-20 mm), semi-carbonation zone (30-35 mm) and non-carbonation zone (40-45 mm).

2.1.2 High CO₂ concentration artificial accelerated climate environments

The samples and experimental environment parameters were summarized in Table 1.

<table>
<thead>
<tr>
<th>Specimens No.</th>
<th>Concrete grade</th>
<th>mix proportions of concrete</th>
<th>T/℃</th>
<th>Relative humidity /%</th>
<th>CO₂ concentration /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1 A2 A3</td>
<td>C20</td>
<td>C:S:G:W=1:0.60:2.30:4.50</td>
<td>20±2</td>
<td>70±5</td>
<td>20</td>
</tr>
</tbody>
</table>

Note: X&T samples were used for XRD and TGA analyses.

Concrete samples

Specimens (prism of size 150×150×450 mm) were cast using plywood molds. After 24 hours, they were removed from the molds and placed in a water bath at 20°C ±1°C for 28 days. Three sets of 100×100×100 mm cubes were also cast following the mixtures shown in Table 1 and followed the same curing regime before measuring the 28 day compressive strength.

At the end of the curing period, the specimens were oven dried at 60°C ±2°C for 48 hours to reduce the moisture content in concrete. They were again sealed in paraffin and stored at 20°C ±2°C for 2 days to reduce the temperature of specimens. At the end of this conditioning regime, three layers paraffin coating were applied on all surfaces of the specimens except for the mold finished top one. This allows a one-dimensional diffusion of carbon dioxide. Then the specimens were subsequently exposed in the climate room at 20 °C and 70% relative
humidity (RH) for 4 weeks to achieve an even redistribution of moisture within the specimens before the accelerated carbonation tests started.

Cementitious materials used were P.O. 32.5 ordinary Portland cement. Their chemical compositions and physical properties of the materials are shown in Table 2. Coarse aggregate of crushed limestone with a maximum size of 20 mm was used. Fine aggregate was river sand with fineness modulus of 2.8. Both aggregates complied with the requirement of ASTM C33.

### Table 2: The chemical compositions and physical properties of cement

<table>
<thead>
<tr>
<th>Chemical composition (%)</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>SO₃</th>
<th>f-CaO</th>
<th>Insoluble residue</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>22.2</td>
<td>5.36</td>
<td>3.43</td>
<td>65.1</td>
<td>2.11</td>
<td>2.42</td>
<td>0.39</td>
<td>0.11</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>Specific gravity (g/cm³)</th>
<th>Loss of ignition (%)</th>
<th>Blaine fineness (cm²/g)</th>
<th>Water requirement (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.21</td>
<td>1.08</td>
<td>3230</td>
<td>100</td>
</tr>
</tbody>
</table>

**Accelerated carbonation test of concrete**

Accelerated carbonation experiments were conducted in the Carbonation Laboratory at the China University of Mining Technology. The temperature, relative humidity and CO₂ levels within the testing room laboratory could be controlled in the ranges of 0-60 °C, 40-95% and 0-50% by volume, respectively. The corresponding accuracies are ±2 °C, ±5% and ±0.1%, respectively. The experimental climate environment condition is 20 °C, 70% of RH and 20% of CO₂ concentration.

For the purpose easy comparison with results in atmospheric environment, samples were cut from the specimens every 6-cm to observe the depth of the totally carbonated zone. Each time after the 6-cm sample was taken out of the concrete, the rest of the concrete was sealed using paraffin and put back to the carbonation laboratory until the another sample from the same concrete was taken 5 days later. The carbonation test stopped and the powder samples were taken from the identical locations where the totally carbonation depth was 28 mm for TGA and XRD analyses when the totally carbonation depth reached 24-30 mm, which is close to those obtained in atmospheric environment.

After the carbonation of the concrete samples, powders were taken from the concrete samples from surface inward for the measurement of pH values and TGA and XRD analyses. For easy comparison, the sampling points were identical to those for the natural environment, i.e., corresponding to the totally carbonated zones with depths of 24 mm, 27 mm, and 30 mm. TGA and XRD analyses were conducted using samples taken at from the concrete with a totally carbonated depth of 28 m. All the samples were analyzed within 48 hours after they were taken from the concrete.

### 2.2 Measurement

#### 2.2.1 pH values in concrete

The samples were ground into powders before mixed with distilled water in a 25 ml beaker at a solid to liquid ratio of 2:1. After the mixture being stored for 10 minutes, the pH value of each sample was measured using a reference combination pH electrode.
2.2.2 XRD analysis

XRD measurements were performed using a D/Max-3B Siemens diffractometer equipped with a Cu(Ka) radiation, Ni filter, graphite monochromator and a proportional detector. The scans were done in the range of $5^\circ$–$65^\circ \ 2(\theta)$. Quantitative XRD diffraction analysis was performed using a program called Original, which is developed to analyze diffraction spectra, composed of broadened Bragg peaks.

2.2.3 TGA analysis

The concentration distributions of calcium hydroxide and calcium carbonate in the depth direction from the surface were measured by thermogravimetric analysis (TGA). Samples were ground into powder while being immersed in alcohol in order to avoid any further carbonation of Ca(OH)$_2$ by air in atmosphere. Then the ground samples were dried and sealed before TGA analyses in the temperature range of 1000$^\circ$C with an increment of 10$^\circ$C/min.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 XRD analysis

Results obtained from natural carbonation and high CO$_2$ accelerated carbonation are shown Figure 2. Figures 2a-1 and 2a-2 show that in the totally carbonation zone (10-20 mm), the phase compositions are nearly identical for samples obtained in natural environment and the artificial accelerated carbonated concrete. They are mainly SiO$_2$, CaCO$_3$ (3.08, 2.926) and Ca(Al$_2$Si$_2$O$_8$) (3.250, 3.199) and MgCa(CO$_3$)$_2$ (3.784, 193). In addition, the XRD peak intensities of the same carbonation products in two environments are close to each other. This indicates that the products of natural carbonation and accelerated carbonation are identical.

From Figures 2b-1 and 2b-2 it can be seen that the variation of pH values in the semi carbonation zone (30-35 mm) in the both main products of natural carbonation and accelerated carbonation were SiO$_2$, CaCO$_3$ (3.080, 2.926), Ca(Al$_2$Si$_2$O$_8$) (3.250, 3.199) and MgCa(CO$_3$)$_2$ (3.784, 193). However, there were also certain amount of Ca(OH)$_2$ (2.643), which was in the zone where Ca(OH)$_2$ and CaCO$_3$ coexist. This indicates that the semi carbonation zone. In addition, the XRD peak intensities of the carbonation products in two different environments were similar to each other, which indicates that the reaction progresses were also similar to each other for both the natural carbonation and the accelerated carbonation.

From Figures 2c-1 and 2c-2 it can be seen that, in the non-carbonation zone (45-50mm), the pH values are nearly constant, the carbonations in these two environments also produced similar phase compositions as indicated by the corresponding XRD peaks. This indicates that the carbonation progress was also similar to each other in both the natural and the accelerated environments. It is worthy to mention that, regardless of natural carbonation and accelerated carbonation, the pH values in the areas right beside the semi carbonation zone (45-50mm) were high and nearly constant. Composition wise, there was still certain amount of carbonation products - CaCO$_3$ (3.0.8, 2.926).

Overall, the above results show that the carbonated concrete samples through natural carbonation and accelerated carbonation had the same phase compositions, similar XRD peak intensities, in the totally carbonation zone or the semi carbonation zone or the non carbonation
All this indicates that the effects of natural carbonation and accelerated carbonation are equivalent.

Figure 2: XRD curve of carbonated concrete
3.2 TGA analysis

The TGA analysis results of the concrete samples obtained after natural carbonation and accelerated carbonation as well as the differential TGA curves are shown in Fig. 3. The relative amount of CaCO$_3$ and Ca(OH)$_2$ in the samples can be estimated from the charts, and they are summarized in Table 3. Figure 3 and Table 3 show that, totally carbonation zone (10-20 mm), there was no Ca(OH)$_2$ detected, which agreed with the XRD results. This indicates that carbonation was complete in this area. In the area (30-35 mm) where pH value varied, there were both Ca(OH)$_2$ and CaCO$_3$. This indicates that carbonation is still in progress – it is the semi carbonation zone. However, limited by the accuracy of sampling, there was a slight difference in the relative amount of Ca(OH)$_2$ and CaCO$_3$ in the concrete samples after natural carbonation and accelerated carbonation. This also agrees with the XRD analysis. Deeper into the surface where the pH values became stable again (45-50 mm), there were CaCO$_3$ in both types of concrete samples after natural carbonation and accelerated carbonation, but this part of CaCO$_3$ is part of the noncarbonated cement slurry.
Table 3: Ca(OH)$_2$ and CaCO$_3$ relative content of carbonated concrete in different depth

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical Composition</th>
<th>Sampling depth</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>10-20 mm</td>
</tr>
<tr>
<td>Natural carbonation</td>
<td>Ca(OH)$_2$</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>CaCO$_3$</td>
<td>100</td>
</tr>
<tr>
<td>Accelerated carbonation</td>
<td>Ca(OH)$_2$</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>CaCO$_3$</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 4 shows the DTA of the non-carbonated ordinary portland cement gel. There was a great amount of CaCO$_3$ in the non-carbonated pure ordinary portland cement gel. This CaCO$_3$ is part of the mixing materials for cement production. Therefore, it can be concluded that, regardless of natural carbonation or accelerated carbonation, the area where pH value is high but stable (45-50 mm) is non-carbonation zone. That is, the depth of carbonation zone and that where pH value varied are the same.

3.2.3 pH Value Distribution of Carbonation Concrete

The change pH values with the carbonation depth in natural environment and accelerated environment are shown in Figures 5 and 6, respectively. The lengths of the semi carbonation zones for both cases are shown in Figure 7. Figures 5 and 6 show that, there were three zones in either natural carbonation or accelerated carbonation, totally carbonation zone, semi carbonation zone and non-carbonation zone. This finding is the same as that reported by Parrot [5]. In the totally carbonation zone, the pH values were 8.3-8.6, whereas they were about 12.5-12.9 in the non-carbonation zone. However, the pH values in the totally carbonation zones were always in a narrow range of 8.3-8.6, regardless of the CO$_2$ levels in the carbonation environments. Then in the semi carbonation zone, the pH value changed linearly, approaching the maximum values.
For the sample obtained in natural carbonation, the totally carbonation depth was $x_a = 24$ mm, 27 mm and 30mm corresponding to the partial carbonation zone of 24-34 mm, 27-36 mm and 30-40 mm, respectively. The lengths of the partial carbonation zones are nearly the same, i.e. 10mm, 9mm and 10 mm, respectively.
For accelerated carbonation, the totally carbonation depth was \( x_a = 24 \text{mm}, \ 27 \text{mm} \) and 30mm and the corresponding partial carbonation zones are in the range of 24-31mm, 27-34mm and 30-38mm, respectively. The lengths of the partial carbonation zones are also nearly the same, 7mm, 7mm and 8mm, respectively. This indicates that, regardless of natural carbonation or accelerated carbonation, the length of the partial carbonation zone was independent on that of the totally carbonation zone. However, the variations of the pH values in the same depths of totally carbonation zone in natural carbonation were higher than those in accelerated carbonation.

Results of experiments show that there were similarities between natural carbonation and accelerated carbonation with respect to both the variation of the pH values in the carbonation zone and the phase compositions. This means that the carbonation results of natural carbonation and accelerated carbonation were compatible, except for the length of the semi-carbonated zone under natural condition was greater than that under the accelerated carbonation. The results of the literature [8] showed that the length of the semi-carbonated zone mainly depends on climate condition (temperature and relative humidity) as well as the properties of the concrete and that the concentration of \( \text{CO}_2 \) and the duration of the carbonation process have no effect on the length of semi-carbonation zone. This discrepancy was caused by the variation of atmospheric condition, such as changes in seasons, day and night, as precipitations. In addition, the properties of the concrete samples were likely also different from each other. All this may contribute to the differences in the experimental results. If everything had been identical, the results should have been the same.

4. CONCLUSIONS

The experimental studies and theoretical analysis indicate that the variations of the pH values as well as the phase compositions produced in the natural carbonation and the accelerated carbonation are compatible, which indicates that the carbonation progresses are the same for both environments. The difference between them is that the length of semi-carbonation zone under high \( \text{CO}_2 \) concentration accelerated climate environments is shorter than that under natural condition. The study indicates that the causes of the difference are climate condition (temperature and relative humidity) and concrete constituents. \( \text{CO}_2 \) concentration and carbonation time have no relation to the length of semi-carbonation zone. It is feasible to study carbonation process of concrete under natural condition by applying the high \( \text{CO}_2 \) concentration artificial accelerated carbonation technique.

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