# Effect of carbonic acid water on the degradation of Portland cement paste: Corrosion process and kinetics

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## HIGHLIGHTS

- Changes of Portland cement paste in carbonic acid water were followed.
- Carbonic acid water corrosion process of Portland cement paste was described.
- A carbonic acid water corrosion model of Portland cement paste was proposed.
- A corrosion kinetics was theoretical deduced and fitted with experimental data.

## ARTICLE INFO

## ABSTRACT

Underground concrete structures usually suffer from carbonic acid water corrosion, thus evaluation and prediction of the carbonic acid water corrosion are very important for cement-based materials. Portland cement pastes were immersed into a renewal carbonic acid water, then the corrosion process was followed in this paper. The results show that no obvious corrosion was observed in the first 7 days, while significant corrosion was observed after 28 days corrosion. The corroded zone can be divided into three regions according to the Ca/Si molar ratio of the cross section, where dissolution of CH, carbonation and dissolution of carbonates, and multi-decalcification of hydration products occurred gradually from the internal to the external. Based on the experimental data, a carbonic acid water corrosion model of Portland cement paste was proposed, then the corrosion kinetics, which can be used to predict the carbonic acid water corrosion of Portland cement paste, was theoretically deduced and fitted using the experimental data.

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## 1. Introduction

In recent decades, more and more underground buildings have been built (e.g. metro, huge building foundation, underground plaza and parking) due to the land shortage, especially in large cities. Certain amount of $CO_2$, either from artificial activities ($CO_2$ geological storage, gas treatment solutions, etc.) or from natural environment (microbial decomposition, geological chemistry and so on), generally dissolute in underground water. Therefore, these underground buildings directly contacted with carbonic acid water, which may results in significant corrosion to the underground concrete structures.

Generally, concrete and cement mortar in carbonic acid water are carbonated from the outside, as the hydration products (mainly $Ca(OH)_2$ and C-S-H gel) can react with $CO_2$ to form calcium carbonate (as shown in Eqs. (1) and (2)) [1–4]. Then the calcium carbonate dissolute and is removed by water flow (as shown in Eq. (3)) [5,6], resulting in a lager porosity and more significant carbonic acid corrosion. The leaching of $Ca^{2+}$ from cement paste in corrosive carbonic water environment also leads to the reduction of pH value of the pore solution [7–9] and consequently to the corrosion of steel bar in reinforced concrete. Therefore, carbonic acid water has a significant influence on the durability of concrete structures [10].

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \tag{1}$$

$$C\text{-}S\text{-}H \text{ gel} + CO_2 \rightarrow Silica \text{ gel} + CaCO_3 \tag{2}$$

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca^{2+} + 2HCO_3^- \tag{3}$$

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In the previous studies, the degradation of cement-based materials under simulative carbonic acid water was evaluated by using various leaching protocols [7,8,11–13]. The results indicated that the leaching processes of $Ca^{2+}$ played a key role in the degradation of concrete. However, the leaching test were mainly conducted in the $NH_4NO_3$ solution [5] or meta-acid nearly neutral carbonated aqueous conditions [8], which are quite different from the real underground carbonic acid water. In addition, the corrosive solution was never changed [14] or periodically renewed [15], which may lead to large deviation or incorrect conclusion.

In order to simulate the real underground carbonic acid water, a special apparatus was employed to generate artificial carbonic acid water, and then Portland cement paste was placed in a continuous renewal carbonic acid water. Changes of chemical and mineral compositions of Portland cement paste during carbonic acid water corrosion were followed, then corrosion process and kinetics were clarified. The results will provide a better understanding of carbonic acid water corrosion and a prediction method to evaluate the corrosion depth.

## 2. Experimental procedures

### 2.1. Raw materials

ASTM type II Portland cement was employed to prepare the cement paste. Its chemical composition and basic physical properties are given in Table 1. Tap water with a constant temperature of $20 \pm 1$ °C was used as mixing water.

### 2.2. Specimen preparation

Portland cement paste was prepared by mixing Portland cement and tap water at a mass ratio of 0.5 homogenously, the paste was cast into $2 \times 2 \times 2$ cm$^3$ moulds and then cured at $20 \pm 1$ °C and 90% relative humidity chamber for 24 h. The demoulded specimens were cured in lime-saturated water at $20 \pm 1$ °C for 27 days.

### 2.3. Carbonic acid water corrosion

A special laboratory apparatus was assembled to simulate real carbonic acid water environment. The apparatus consisted of three major parts (as shown in Figs. 1 and 2): (1) Carbonic acid water preparation chamber, (2) Corrosion reaction tank, and (3) Controlling and recording devices. The $CO_2$ concentration and the pH of carbonic acid water were controlled by the $CO_2$ pressure in the chamber. The finely sealed corrosion tank was connected with the carbonic acid water preparation chamber by a stainless vessel, so the $CO_2$ pressure of these two chambers was maintained the same. To keep the $CO_2$ concentration constant and remove the $Ca^{2+}$ in carbonic acid water, the carbonic acid water in the reaction tank was removed and replaced at a constant speed of 2 L/h, which means that the carbonic acid water (about 40 L) in the reaction tank can be renewed per day.

To simulate the carbonic acid water corrosion of underground concrete structures, the temperature was chosen as $14 \pm 1$ °C, the $CO_2$ concentration of the carbonic acid water was maintained 340 ± 20 mg/L by setting the $CO_2$ pressure at 0.1 MPa, and the pH value of the carbonic acid water was kept in the range of 4.5–4.6. Only one surface of specimens was immersed into the carbonic acid water, while other surfaces were pre-covered using epoxy. During the corrosion experiment, the temperature, pH value and $CO_2$ concentration of the carbonic acid water were on line monitored and adjusted to the target value as shown in Figs. 3 and 4.

### 2.4. Testing methods

After 3, 7, 14, 21, 28, 42, 60, 90, 120 and 180 days corrosion, the specimens were taken out and observed by optical microscope (OLYMPUS SZX10), then specimens were dried in a vacuum oven at 45 °C for 48 h and the surfaces of the specimens were observed again. Mass loss of the specimen before and after corrosion was also followed by Eq. (4):

$$m_l = \frac{m_o - m_c}{m_o} \times 100\% \tag{4}$$

where: $m_l$ (%) is the mass loss of the specimen during corrosion; $m_o$ is the mass of the specimen before corrosion (oven dry); $m_c$ is the mass of the specimen after corrosion (oven dry).

The specimens were cut along with the corrosion direction, then the cross section was observed by optical microscope and scanning electron microscope (SEM). The mineral composition of corroded sections was characterized by X-ray diffraction (XRD) and differential scanning calorimetry-thermogravimetry (DSC-TG, heating rate of 10 °C/min in $N_2$ atmosphere). Samples for SEM, XRD and DSC-TG were prepared according to the literature [16]. Linear energy dispersive spectrometer (EDS) scanning was employed to determine the Ca/Si molar ratio of the corroded sections, then the corrosion depth was measured according to the Ca/Si molar ratio change.

## 3. Results

### 3.1. Morphological observation

As shown in Fig. 5, no obviously corrosion was observed for specimens immersed in carbonic acid water for 7 days. In contrast, significant corrosion was observed for specimens after 28 days corrosion. Notably, more and more cracks were seen on the surface of specimens as corrosion time proceed, and the width of cracks became lager, especially for specimens after drying.

The optical photographs of cross section of Portland cement paste after corrosion are shown in Fig. 6. The depth of cross section increased as the corrosion time proceed. According to the color change, the cross section could be divided into three regions (region I, II and III) from surface to internal cement matrix. Obviously boundary lines between region I, II and III were seen in Fig. 6, while the boundary line between region III and cement matrix was relatively obscure. The thickness of region I and region II increased dramatically with the increase of corrosion time. In addition, region I was easily detached from the specimens due to large amount of cracks, especially for specimens after 90 days corrosion.

**Table 1**
Chemical composition and physical properties of Portland cement used.

| Specific density (g/cm$^3$) | Specific surface area (m$^2$/kg) | Chemical composition (%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO | SO$_3$ | MgO | LOI | Others |
| 3.11 | 438 | 21.2 | 5.4 | 5.03 | 62.07 | 2.60 | 1.25 | 2.23 | 0.13 |

*Note:* LOI, loss on ignition.