The variation of pore structure in cement paste exposed to sodium sulfate solution with an in-suit X-ray CT testing technology

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Abstract. In this paper, the variation of compressive strength of cement paste specimens under external sulfate attack was studied. Then the microstructure characteristics of the cement attacked by sodium sulfate solution was observed by the Scanning Electron Microscope (SEM) test. Subsequently, an in-suit X-ray CT testing technology was used to monitor the change of pore structure in cement paste specimens under different exposure time, and the Avizo software was used to calculate the porosity of cement paste specimens and porosities of different depth zones in cement paste specimen. The results show that the compressive strength increases firstly and then decreases. Owing to that ettringites are produced in cement paste specimens, and the number and the volume of ettringites increase with the increase of exposure time. Leading to that the porosity of cement paste specimens decreases first and then increases with the increase of exposure time. And the porosities of different depth zones undergo a process of decreasing first and then increasing from surface to interior in cement paste specimens. It indicates that the deterioration process is from the surface to the interior with the increase of exposure time.

1. Introduction
The durability of cement-based material is a major issue in structural engineering over the last decades [1]. In recent years, the increasing amount of cement-based material used in marine environment or in underground water leads to a higher requirement for the durability. As known, sulfate as a corrosive media, was one of the most destructive objectives for cement-based material [2, 3]. Therefore, the studies on deterioration mechanism and properties variation of cement-based material caused by sulfates had been conducted for the last decades.

As to the chemical shrinkage, dry shrinkage, autogenous shrinkage and loading, cement-based material inevitably produced micro-cracks [4, 5]. When cement-based material contacted with sulfate ions solution, sulfate ions transport into cement through the micro-cracks and pore structure from the high concentration area to the low concentration area [6, 7]. Studies [8, 9] pointed that the external sulfate ions reacted with the cement hydration products to generate ettringite and gypsum, which was regarded as the expansive products. The volume change of expansive products in cement-based materials is mainly due to the change of the production of ettringite and gypsum [2, 10]. When the growth of expansive products were limited by the micro-pore structure and the crack, the swelling stress appears. Then the swelling stress gradually exceeded the strength of cement-based material, causing swelling and cracking, which was resulted into the change of the porosity. Moreover, the new
generating micro cracks accelerated the transport of sulfate ions and the deterioration process of cement-based material. The deterioration of cement-based materials caused by external sulfate corrosion is a process from the surface to the interior. However, the existing studies only analyze the deterioration of cement-based materials caused by expansive products qualitatively.

In this paper, the compressive strength of cement paste specimens under external sulfate attack were measured by the uniaxial compression test. Then the microstructure characteristics of the corroded cement paste specimens were observed by SEM test. Finally, an in-suit X-ray CT testing technology was used to monitor the variation of pore structure over exposure time.

2. Experiments and Method

2.1. Materials and sample preparation
In this paper, the P·I 52.5 cement was used for the experiment. The chemical composition is shown in Table 1 and the mineral composition is shown in Table 2. Sodium sulfate (Na$_2$SO$_4$) was used as the corrosion medium in solution with the mass concentration of sulfate ion of 5% (molar concentration was 352 mol/m$^3$).

| Composition | LOI | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO | MgO | SO$_3$ | K$_2$O | Na$_2$O |
|-------------|-----|---------|-------------|-------------|-----|-----|--------|-------|--------|
| Mass fraction (%) | 0.77 | 20.87 | 4.87 | 3.59 | 64.47 | 2.13 | 2.52 | 0.65 | 0.11 |

| Composition | C$_3$S | C$_2$S | C$_3$A | C$_4$AF |
|-------------|--------|--------|--------|---------|
| Content (%) | 63.94 | 16.79 | 7.41 | 11.86 |

The water-cement ratio (w/c) was selected as 0.35 with a dimension of 20 mm × 20 mm × 40 mm. The specimens were kept under laboratory conditions (20 ± 5 °C) for 24 h before demolding, then cured for 28 d with the temperature of 20 °C and relative humidity of 95%. The cement paste specimens were soaked in the sodium sulfate solution at 20 ± 2 °C and the sodium sulfate solution was replaced every 3 d during the corrosion process to ensure a constant concentration of Na$_2$SO$_4$.

2.2. Uniaxial compression test
The uniaxial compression test was conducted by the Microcomputer controlled electro-hydraulic servo pressure testing machine (Zwick/Roell Z050) made in Germany with maximum loading of 50 kN and loading speed of 0.5 mm/min. Twenty-five cement paste specimens were divided into five groups for the uniaxial compression test and each group contained five specimens. The corrosion time are 0d (G1), 30d (G2), 60d (G3), 120d (G4) and 180d (G5) respectively. The maximum and minimum compressive strengths acquired from the test were eliminated in each group with other three left in order to increase the effectiveness of the data.

2.3. SEM Test
The field emission environmental (FEG) SEM (Quanta250) manufactured by FEI Co., USA was used to observe the change in micromorphology of cement paste specimen immersed in 5 wt.% Na$_2$SO$_4$ solution. The cement paste specimens were used for SEM with the exposure time of 0d, 60d and 180d and the samples were 3mm × 3mm × 3 mm cube cut off from the corner of the corroded specimen.

2.4. In-suit X-ray CT testing technology
2.4.1. X-ray Computed testing technology. The in-suit X-ray Computed Tomography (X-CT) test was conducted by Micro X-ray CT instrument. The X-ray projections were acquired with an exposure time.
of 0.32s at an accelerating voltage of 150 kV and 140 μA beam current using a tungsten target. For the in-suit CT test, one cement paste specimen was used to obtain the pore structure of cement paste with corrosion periods of 0 d, 60 d and 180 d.

2.4.2. Establishment of the Three-Dimensional Structure. The Avizo software package was used to segment, generate and visualize the three-dimensional (3D) structure from the X-ray CT test. Median filtering was utilized to improve the quality of images. Then the threshold intensity segmentation method was used to distinguish and quantify the pores and matrix in cement paste. The threshold value of intensity was selected as 72.1. Figure 1(b) and Figure 2(a) show two dimensional (2D) slice of cement paste specimen with exposure time of 60 d before and after the threshold segmentation. The black parts in Figure 1(a) and the blue parts in Figure 1(b) are the pore structure, and the other parts are cement paste material.

![Figure 1](image1.png)
(a) Gray image of 2D slice  (b) 2D slice image after threshold segmentation

**Figure 1.** 2D slice of cement paste specimen before and after the threshold segmentation.

The sulfate ions gradually spread from the surface to the inside of cement paste samples, causing gradual corrosion of cement paste specimens. In order to study the variation of pore structure in different depth zones of cement paste specimens with the increase of exposure time, the cement paste specimens are divided into five zones from the outside to the inside. The diagram of the division of the cross section zones is shown in Figure 2. Moreover, the height of the longitudinal section of the specimen is twice the width of its cross section.

![Figure 2](image2.png)

**Figure 2.** The diagram of the division of the cross section zones.

In order to acquire 3D pore structure of each section in cement paste, marching cube algorithm was used to extract the triangular surface patches from the date of binary images. Then, the triangular surfaces were rendered by illumination model and the 3D structure of cement paste generated. Figure 3 shows 3D structure of pore in cement paste specimen with exposure time of 60d.
2.4.3. The calculation of porosity in different cement zones based on the X-ray CT test. Based on the 3D structure of cement paste, the porosity of cement paste can be calculated by Avizo software according to the number pixels of pore structure and cement paste, as follows:

$$\phi = \frac{n_p}{n} \times 100\%$$  \hspace{1cm} (1)

Where $\phi$ is the porosity of cement paste specimen, $n_p$ is the pixel number of pore structure; $n$ is the pixel number of specimen.

Porosity can also be calculated according to the volume ratio of the pore structure and the cement paste specimen, as shown in equation (2):

$$\phi = \frac{V_p}{V}$$  \hspace{1cm} (2)

Where $V_p$ is the volume of pore structure, $V$ is the volume of cement paste specimen.

In order to obtain the porosity of different zones in cement paste specimen, the porosity of zone 5 can be calculated according to Eq. (3).

$$\phi_5 = \frac{n_{p5}}{n_5} \times 100\%$$  \hspace{1cm} (3)

Then the total porosity of zone 4 and zone 5 can be obtained by Eq. (4).

$$\phi_4' = \frac{n_{p4}}{n_4} \times 100\%$$  \hspace{1cm} (4)

Where $\phi_4'$ is the total porosity of zone 4 and zone 5, $n_{p4}$ is the total pixel number of pore structure in zone 4 and zone 4, $n_4'$ is the total pixel number of zone 4 and zone 5.

According to Eq. (2), the total porosity of zone 4 and zone 5 can also be calculated as follows.

$$\phi_4' = \frac{V_{p4} + V_{p5}}{V_4 + V_5}$$  \hspace{1cm} (5)

Where $V_{p4}$ and $V_{p5}$ are the volume of pore structure of zone 4 and zone 5 respectively, $V_4$ and $V_5$ are the volume of zone 4 and zone 5 respectively.

According to Eq. (4) and Eq. (5), the porosity of zone 2 can be calculated as follows.
Adopting the same method, we can calculate the value of $\phi_3$, $\phi_2$ and $\phi_1$.

3. Results and Analysis

3.1. Variation of compressive strength with the exposure time

Figure 4 shows the variation of compressive strength with the increase of exposure time. As it can be seen that the compressive strength of cement paste specimens increase rapidly at an early stage. The compressive strength reaches the peak value at 60d with the value of 75.7 MPa. Then, the the compressive strength tends to decrease. The value at 180d is 51.1 MPa, which is lower than the value as 54.7 MPa at 0d. With the increase of exposure time, the downward trend becomes more evident.

![Figure 4. The variation of compressive strength with the exposure time.](image)

3.2. Change in micromorphology

Figure 5 shows the SEM images of the cement paste specimens. In Figure 5 (a), it can be found that many micro cracks and micro pores exist in the cement paste specimen, which provide transport channels for sulfate ions into interior cement [6]. Figure 5 (b) and Figure 5 (c) show that a amount of needle-like ettringite crystallites in micro cracks and micro pores of cement at the exposure time of 60d and 180d. The ettringite fills in micro-cracks and micro-pores, leading to the increase of compactness, which leads to the increase in the compressive strength of concrete at micro-scale. With the continuous precipitation of ettringite in micro-pores and micro-cracks, the volume of ettringite reaches a certain level that causes the expansion stress in the pore wall of the cement matrix. Then the cement swells and cracks, leading to new micro-cracks and reducing the compactness of concrete. These are microscopic mechanisms of the reduction of mechanical properties of concrete under external sulfate attack at macroscopic scale.

![Figure 5. The microstructures of cement paste with different exposure time.](image)
3.3. Analysis of pore results of cement specimens based on X-ray CT test

Table 3 shows the porosities of different cement depth zones. It can be found that the total porosity of cement paste specimen decreases first and then increases with exposure time. The porosities in zone 1, zone 2 and zone 3 also undergo a process of decreasing first and then increasing. The porosity in zone 4 decreases slowly. Comparing with the porosity of zone 5 at 0d, the value changes little at 60d, but decreases at 180d. The variation trend of porosity indicates the deterioration process is from the outside to the interior with increase of exposure time. Sulfate ions transport into cement and react with cement hydration products to generate ettringite. As it is known in section 3.2, the volume of ettringites increases with the exposure time, leading to the change of pore structure and compactness of cement. Initially the expansive products play a role in filling pores, which makes the porosity of cement paste decrease. However, as the expansion products continue to increase, the volume exceeds pore volume, it will cause the expansion of the pore, resulting in the increase of porosity. This phenomenon initially occurred in the outer layer of the specimen, but with the increase of exposure time, the inner region also gradually experienced a process of porosity first decreasing and then increasing. Which is the microscopic mechanism of the change of compression strength at macroscopic scale.

| Zone | Total | 1    | 2    | 3    | 4    | 5    |
|------|-------|------|------|------|------|------|
| 0d   | 0.119 | 0.109| 0.123| 0.133| 0.135| 0.146|
| 60d  | 0.089 | 0.079| 0.091| 0.1  | 0.124| 0.145|
| 180d | 0.135 | 0.141| 0.135| 0.134| 0.094| 0.108|

4. Conclusions

(1) The compressive strength of cement paste specimen soaked in Na$_2$SO$_4$ solution decrease after the initial enhancement.

(2) The microstructure analysis of SEM shows that ettringite form in pores and cracks. The number and the size of ettringite increase over time within 180d.

(3) The variation trend of porosity indicates that the deterioration process is from the surface zone to the interior zone with the increase of exposure time.

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