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Study on accelerated microbial corrosion of concrete by artificially intensified sewage

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ABSTRACT

In this study, the artificially intensified sewage with different levels of chemical oxygen demand (COD) were prepared, and the changes in weight and strength, as well as the micro morphology, mineral compositions and pore structure of concrete specimens immersed in the artificially intensified sewage and water were investigated in comparison. In parallel, the COD, pH, H_2S and O_2 values, as well as the microbial species and contents of sewage were monitored in the corrosion process. Furthermore, the microbial structure and activities within biofilm developed on concrete surface were also analyzed. The results indicated that the increase of COD concentration of sewage from 300 to 9000 mg/L led to the decline of sewage pH from 6.4 to 2.3 and increase of biofilm thickness from 300 to 800 μm, as well as the substantial growth of dominant microorganisms (Bacteroidete, Proteobacteria, etc.). The drop of pH level and O_2 concentration within biofilm also indicated the high activities of sulfate-reducing and sulfur-oxidizing reaction. Correspondingly, after 150 days of immersion both the mass loss and strength decline rate of concrete increased from 0.32% to 1.78% and from 10.6% to 31.7%, respectively. Furthermore, the microstructure of the specimens in sewage became loose and porous. The CH content of specimens in sewage was significant lower than that of specimens in water, and both the cumulative mercury quantity and harmful macropore proportion of specimens in intensified sewage were significantly larger than that of specimens in water, which indicated the chemical reaction between CH and some acid substance*. Overall, the sewage concentration increased by 30 times can triple the corrosion rate of concrete. The results obtained are expected to explore a fast and realistic method to simulate the concrete corrosion in full flow sewer pipes.*

Keywords: artificial sewage; biofilm; concrete; microbial corrosion; pore structure; strength

1.0 INTRODUCTION

Reinforced concrete has been widely used in municipal infrastructure projects, such as sewage pipelines, wastewater collection and treatment facilities, etc. These structures are generally at underground or semi underground, and long-termly subjected to the acid, erosion, microbial and other corrosive attacks, thus resulting in the deterioration of concrete. The corrosion of concrete sewer pipes is one of the most serious problems in sewerage works today (Jensen *et al.*, 2009; Vollertsen *et al.*, 2008). In Los Angeles County, approximately 10% of the sewer pipes are subject to significant corrosion, and the rehabilitation costs are as high as $400 million (Zhang *et al.* 2008). The restoration of the overall damaged sewer systems in Germany is estimated to cost about €100 billion per year (Sydney *et al.* 1996). Not only the construction and replacement of sewer pipes is very expensive, but the failure of sewer pipes causes extensive damage to roads and pavements. Therefore, it is necessary to improve the durability of concrete in sewage environment.

In non-full flow sewers, much of the deterioration of concrete is the result of microbial induced corrosion. As early as in 1945, it had been discovered that bacteria were involved in the deterioration of internal sewer concrete, and the corrosion mechanism was proposed as a result of the sulfur cycle (Parker, 1945). Under the anaerobic condition, sulfate reducing bacteria (SRB) are present in the sewage and produce hydrogen sulfide (H_2S) from sulfur compounds. Once H_2S escapes into the sewer atmosphere, it can react with oxygen to form elementary sulfur, and subsequently, to form sulfuric acid by sulfur oxidizing bacteria (SOB), which causes the formation of expansive products such as gypsum and ettringite (O'Connell *et al.*, 2010). Moreover, the thiobacillus activity could be increased due to the high concentrations of H_2S, moisture and oxygen, and thus the deterioration of concrete could be aggravated (Gadekar *et al.*, 2006).

The methods for studying the corrosion of sewer concrete can be divided into two categories: in situ corrosion test and accelerated corrosion test. The in situ test, in which the concrete specimens were installed in a real sewer system or the small concrete cores were drilled from the internal sewer pipeline to investigate the corrosion process under complex sewage condition, is the most direct research method (Scrivener and Belie, 2013; Alexander *et al.*, 2011). However, it often needs a couple of years or even decades of tracking and monitoring. Moreover, the actual sewer conditions vary with the region and climate, thus the results obtained have limitation. Over the years, several accelerated methods have been developed to simulate the deterioration of concrete in sewage. Chemical test, that is, to simulate the sewage corrosion environment with aggressive chemical medium. In view of the proven corrosion mechanism, the most commonly used chemical media are sulfuric acid (Yuan *et al.*, 2013; Durning and Hicks, 1991) and sulfate solution (Gollop and Taylor, 1996; Djuric *et al.*, 1996). To simulate microbial induced corrosion occurred in sewers, several researchers took cultivated media with large number of bacteria as corrosive medium, and established the test protocol which can provide optimum conditions (temperature, nutrients) for the bacteria. So far most researches are carried on the corrosion of concrete by Thiobacillus culture medium (Sand and Bock, 1987; Yousefi *et al.*, 2014; Aviam *et al.*, 2014; Bielefeldt *et al.*, 2009). In China, due to the reality that small-diameter pipes are used for sewage system, many gravity sewers, which were built in the 1980s and 1990s, are under full flow operation condition with the increase of sewage discharge, and they were also suffered severe corrosion.

In this study, the artificially intensified sewage with different concentration was prepared to accelerate the test, and the changes in weight, strength and surface roughness of concrete specimens in sewage and clean water were investigated comparatively. The experiments were conducted over a period of 150 days. The deterioration of specimen was also evaluated by a number of techniques including scanning electron microscopy (SEM), mercury intrusion porosimetry (MIP), X-ray diffraction (XRD) and thermo-gravimetric analysis (TGA). In parallel, the pH, COD, O_2 and H_2S values of sewage were monitored in the corrosion process, the microbial species and contents of artificial sewage with different concentration were also measured. Furthermore, the microbial structure and activities within biofilm developed on concrete surface were also analyzed by using confocal scanning laser microscopy (CSLM) and microelectrode. The results obtained are expected to explore a fast and realistic method to simulate the concrete corrosion in full flow sewers and enrich our understanding of the microbiol induced concrete corrosion.

2.0 EXPERIMENTAL PROGRAM

2.1 Concrete specimens

The concrete specimens with a dimension of 40×40×40 mm^3 were prepared for various tests. The materials used were Grade 42.5 Ordinary Portland Cement, river sand with a fineness modulus of 2.8 and an apparent density of 2.61 g/cm^3, and limestone aggregate with an apparent density of 2.64 g/cm^3 and particle size between 5 and 10 mm. The concrete mixture with a water/cement ratio of 0.5 was composed of 384 kg cement, 594 kg sand and 926 kg limestone aggregate per cubic meter. After curing (at temperature 20 °C and relative humidity 95+%) for 28 days, the original macroscopic properties of specimens were tested firstly, and then the specimens were placed in sewage and clean water, respectively, to make a comparative study. The corrosion process was monitored by investigating the performance of concrete at different immersion times (30, 60, 90, 120 and 150 days).

2.2 Artificially intensified sewage

The artificially intensified sewage was prepared as follows: first, activated sludge was taken from the Sewage Plant as the parent, then nutrient solution was added, which were produced by adding right amount of carbon source, nitrogen source, mineral elements, growth factor, etc., to promote the reproduction of microbes. Generally, the chemical oxygen demand (COD) of the municipal sewage, which can reflect the relative content of the organic substance, is about 300 mg/L. And there is a direct link between the COD value and the degree of the sewage induced corrosion of concrete. After a series of calculation and adjustments, three types of intensified sewage were prepared, and their COD concentrations were as high as 10, 20 and 30 times of ordinary sewage, respectively. Table 1 shows the compositions of the nutrient solution. During the experiment, the nutrients should be added periodically (once every 7 days) to maintain the stability of sewage concentration. In addition, the temperature of the sewage was controlled at 30 ℃ to guarantee the growth of microbes.

Table 1. Compositions of the nutrients (g/20 kg nutrient solution)

Sewage sample	SC1	SC1	SC1	SC1
Starch	12.0	125.0	200.0	307.2
Glucose	6.0	62.0	110.0	167.7
Peptone	6.0	14.0	28.5	46.4
Urea	4.0	8.0	12.0	20.0
$(NH4)_2HPO_4$	1.8	4.5	6.7	5.6
$MgSO_4$	1.3	2.4	3.6	3.0
NaCl	0.6	1.0	1.2	1.5

2.3 Simulation chamber for sewage corrosion

An in-house device, which can simulate the corrosion of artificial sewage on concrete, shown in Fig. 1, was used for accelerated corrosion test in this study. Each reactor was formed with a plexiglass cylinder (400 mm inner diameter with 8 mm thick wall). There was a cover to seal the reactor and an automatic heating rod was placed to keep the sewage at a constant temperature. Moreover, to prevent the sedimentation of sewage and maintain a uniform and stabilized corrosive environment, a mixer was fixed on the center of the device. And the medium inside the chamber was replaced by the fresh nutrient solution every seven days using a pump. The total liquid volume removed per cycle was less than 30% of the original volume of sewage. Concrete specimens were placed on the shelf and immersed in the sewage, thus each surface of the specimens could be corroded fully and evenly. In this research, four simulation chambers were required to fill with sewage of different concentrations.

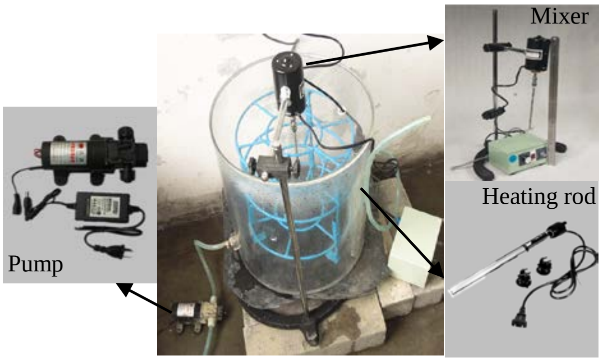

Fig. 1. In-house simulation chamber for sewage corrosion test

2.4 Test methods

<u>Macroscopic performance of concrete</u>
The mass change of specimens was determined by gravimetric method measured by a digital balance with the resolution of ±0.01g. Every time before weighing the specimens was washed using clean water resulting in the saturated surface dry status. The measurement was repeated for at least three times and the results were the average of measured data. The compressive strength of fine aggregate concrete was tested according to Chinese standard of "*Method of testing cements-Determination of strength*" (GB/T 17671-1999), and the results were the average of six values at the same run.

<u>Microscopic performance of specimens</u>
In order to investigate the deterioration of concrete microstructure, the SEM micrographs of the surface specimens were obtained after being immersed in sewage with different concentrations for 90 days. The specimens in clean water were also analyzed for comparison. The image was magnified 5000 times. Besides, some samples from the surface layer were analyzed using MIP to study the pore structure, and others were grinded using an agate morear for XRD and TGA analyses. The XRD measurements were performed using a Bruker D8 diffractometer. Spectra were obtained in the range of 4°＜2θ＜60°. For TGA measurement a sample of 150 mg was heated in a N_2 atmosphere at a rate of 10 C/min.

<u>Water indicators of artificial sewage</u>
The main indicators of the sewage were measured by using a multi-parameter water quality analyzer (WDC-PC02). The test methods, which are based on the Chinese standard of "*Method for the examination of municipal sewage*" (CJ/T 51-2004), were executed as follows: The pH was directly determined using a pH electrode. The COD concentrations were determined by the potassium dichromate titration method. The dissolved oxygen was determined by iodimetry. The concentrations of T-H_2S (defined as the sum of H_2S, HS^- and S^{2-}) were determined by the methylene blue spectrophotometry. In addition, to study the diversity of microorganisms in artificial sewage, the DNA sequencing of sewage was carried out by the Miseq high throughput technique, and the data obtained were analyzed using Mothur and QIIME software.

<u>Microbial structures and activities in biofilm</u>
Concrete specimens with attached surface biofilm were removed from sewage and dipped in buffer solution, consisting of NaCl (137 mmol/L), KCl (2.7 mmol/L), Na_2HPO_4 (4.3 mmol/L) and KH_2PO_4 (1.4 mmol/L), to rinse off the loose cells. The biofilm was stained in the diluted rhodamine red fluorescent staining solution and incubated for 1 h at room temperature. After rinsed for one more time, the microbial community structures of biofilm were visualized under Fluoview FV-1000 CLSM. The wavelengths of excitation photon and emission photon are 543 nm and 591 nm. For microelectrode measurement, the concrete specimens were placed in the sewage, and the in situ steady-state concentration profiles of pH and O_2 in the biofilms were measured, using Unisense microelectrode testing system. At least three concentration profiles were measured for each biofilm specimen.

3.0 RESULTS AND DISCUSSION

3.1 Monitoring parameters of sewage

In this study, to maintain a stable corrosion environment, about one third of the sewage in the reactor was replaced with the nutrient solution periodically once every 7 days. The main sewage parameters were tested before and after sewage replacement every time. The whole monitoring duration was 5 months.

COD

The measured CODs of the sewage with different concentrations are shown in Fig. 2. It can be seen that in every period of sewage replacement, the COD values of sewage decreased gradually with the time, which was due to the effects of microbes on degradation of organic matter in sewage. After adding nutrients periodically, the COD values of sewage can rise back to the initial levels. The higher the initial COD value was, the greater the drop of COD would be. For sewage samples of SC1, SC2, SC3 and SC4, which had initial COD values of 300, 3000, 6000 and 9000 mg/L, the reductions of their COD were 120, 1900, 3700 and 5400 mg/L, respectively. It can be concluded that the sewage with a high COD concentration also contained more microorganisms.

pH

Fig. 3 shows the evolution of sewage pH value over time. It can be seen that all the initial pH values of sewage with different concentrations were about 7.3. For sample SC1 with COD of 300 mg/L, the pH value presented a slightly increase fluctuation in the first ten cycles, which may be due to the dissolution of alkaline product in cement mortar, and then it decreased with a slow speed to 6.5. For intensified sewage samples, all their pH values decreased rapidly during the first cycle, and then varied in wave-type mode gradually going down. After 150 days, the final pH values of sewage SC2, SC3 and SC4 were reduced to 3.4, 2.5 and 2.3, respectively. This demonstrates that with the increase of COD concentration, the sewage was stronger in acidity. So it can be inferred that the high content of organic substance in sewage promoted the growth of the microbes, and the increase of metabolic acid substance could accelerate the corrosion of mortar.

T-H_2S

Fig. 4 shows the evolution of sewage T-H_2S in the test. It can be seen that all the initial T-H_2S values were about 0.93 mg/L, and they increased gradually with time in each cycle, but had a drop after sewage replacement. This can be explained as follows. The fresh sewage contained a large amount of dissolved oxygen, which was not suitable for the survival of anaerobic bacteria. With the consumption of oxygen in sewage, the growth of SRB made the sulfate reduced to hydrogen sulfide. And the high concentration of COD promoted the biochemical reaction in sewage. However, periodically replacing sewage can cause some loss of hydrogen sulfide. Overall, the concentrations of T-H_2S increased gradually with time, especially in the first four cycles. Moreover, the higher the COD of sewage was, the more the growth of T-H_2S would be. Finally, the T-H_2S concentrations of sewage SC1, SC2, SC3 and SC4 increased to 2.56 mg/L, 2.90 mg/L, 2.97 mg/L and 3.01 mg/L, respectively.

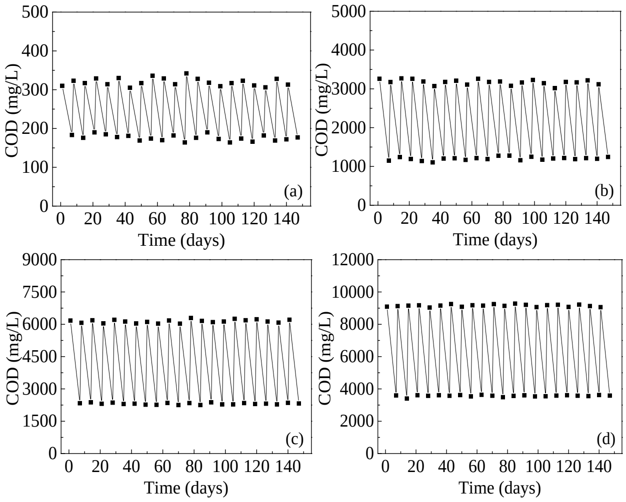

Fig. 2. Evolution diagrams of COD values of sewage with different concentration: a) SCI; b) SC2; c) SC3; d) SC4

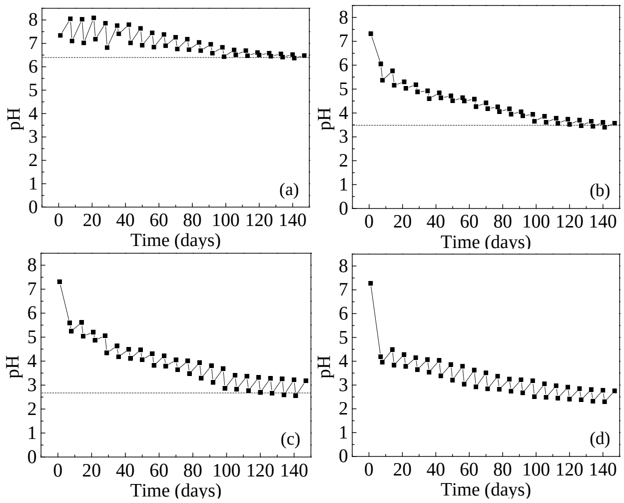

Fig. 3. Evolution diagrams of pH values of sewage with different concentration: a) SCI; b) SC2; c) SC3; d) SC4

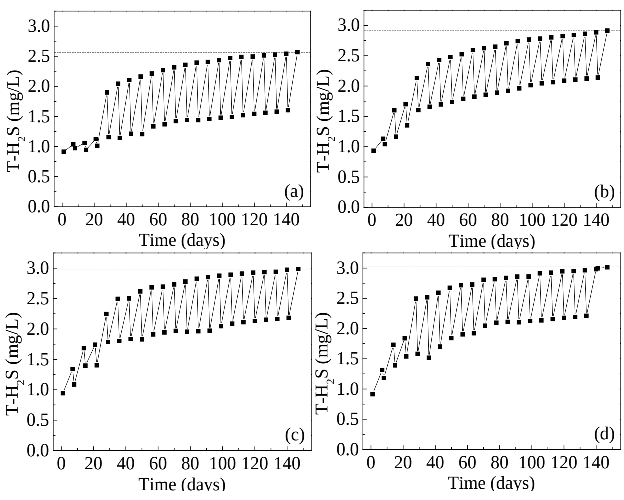

Fig. 4. Evolution diagrams of T-H_2S values of sewage with different concentration: a) SCI; b) SC2; c) SC3; d) SC4

Dissolved oxygen

Fig. 5 shows the evolution of dissolved oxygen concentration of sewage over time. It can be seen that with the increase of COD concentration, the initial oxygen concentration of sewage increased as well. However, the oxygen concentration of the sewage decreased gradually with time, and the drop was greater while increasing the sewage COD concentration, which was due to the oxygen consumption by microbial respiration. After replacing sewage periodically, the dissolved oxygen concentration can have some increase. After about 3 months, the dissolved oxygen contents of intensified sewage samples showed a trend of stabilizing. This may be attributed to the increase of oxygen due to sewage replacement and the consumption of oxygen due to microbial respiration reach a dynamic balance.

Microbe species and content

The DNA sequencing results of sewage with different COD concentration are shown in Fig. 6. It can be seen that there was a high diversity of microbes in sewage at phylum level, which can include 20 phyla or above. Among them, Bacteroidete, Proteobacteria, Firmicutes and Actiobacteria were the dominant microorganism whose relative abundance was approximated 90%. With the increase of COD concentration of sewage, the abundances of dominant microbes grew remarkably. It is clear that a large amount of organic matter in sewage promoted the growth and reproduction of microorganisms. As we know, both Desulfovibrio and Xanthomonas Desulphurization, which were included in Bacteroidete, as well as δ-Proteobacteria, all belonged to SRB. Biological sulfuric acid that the metabolite of SRB, was the main cause of microbially induced concrete corrosion (MICC). Moreover, Escherichia coli and Salmonella, which were included in Proteobacteria, can produce some organic acids, carbon dioxide, etc. in the process of metabolism, which also caused the corrosion of concrete. Therefore, the artificially intensified sewage can be used as effective medium for accelerating the corrosion of concrete.

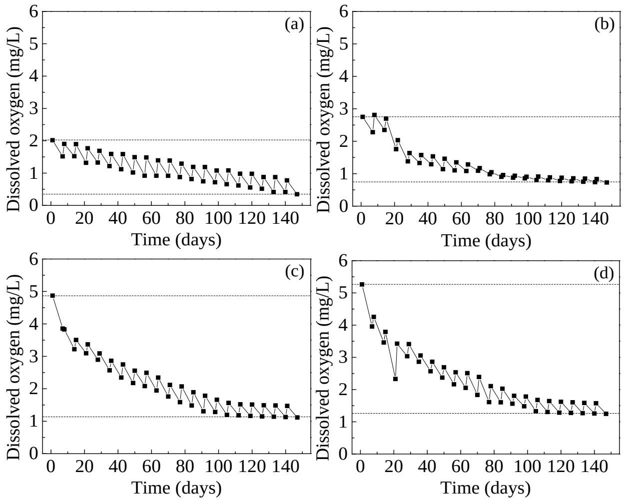

Fig. 5. Evolution diagrams of O_2 values of sewage with different concentration: a) SCl; b) SC2; c) SC3; d) SC4

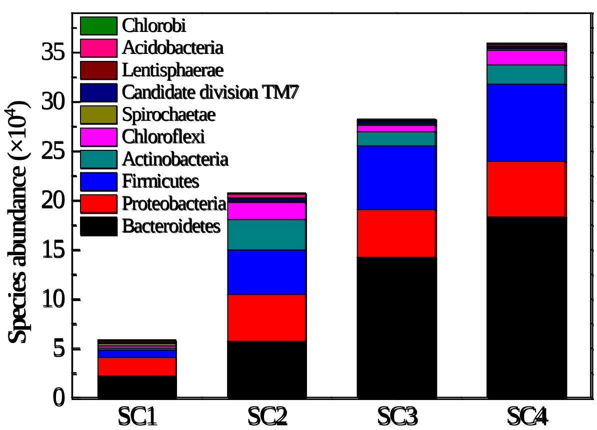

Fig. 6. Distribution of species number at the phylum level of sewage with different concentration

3.2 Microbial structures and activities in biofilm

To further understand the corrosion mechanism of intensified sewage on concrete, it is necessary to investigate the microbial structure and activities in sewage environment, which are responsible for the MICC. The biofilms developed on concrete specimens, which were immersed in sewage with COD concentrations of 300 mg/L, 3000 mg/L, 6000 mg/L and 9000 mg/L, are designated as BC1, BC2, BC3 and BC4, respectively.

Microbial structures in biofilm

The CLSM images of biofilms (at the same depth of 10 μm from biofilm surface) in sewage with different COD concentration are shown in Fig. 7.

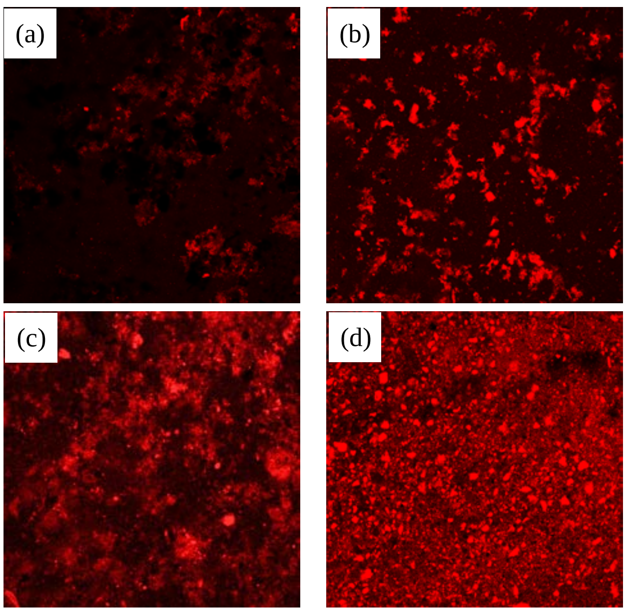

Fig. 7. CLSM images of biofilms in sewage: a) BC1; b) BC2; c) BC3; d) BC4

It can be seen that with the increase of sewage concentration, the number of microorganisms within biofilm increased as well. Thus, it is clear that the high content of organic substance in sewage can provide adequate nutrition for the microorganisms, and greatly promote their growth and reproduction.

Microbial activities in biofilm

Steady-state concentration profiles of pH and O_2 in the biofilms were measured with microelectrode, as shown in Fig. 8. After 30 days of immersion of the concrete specimens in sewage with different COD concentration, the thickness of the biofilm BC1 was about 300 μm, and with the increase of sewage concentration, the biofilm grew thicker, the thickness of biofilm BC4 had increased to 800μm.

In addition, when the COD concentration of sewage increased from 300 to 9000 mg/L, the pH level of biofilm fell from 6.3 to 3.7, indicating that the increase of acid substance. Moreover, the O_2 concentration drastically decreased by mainly an oxygen consumption process and the anaerobic zones can be found in the intensified sewage biofilms (BC2, BC3 and BC4). This may be likely that dissolved H_2S was oxidized in the biofilm and subsequently pH decreased. With the increase of sewage concentration, the large amounts of organic compounds and microorganisms promoted the sulfate-reducing and sulfur-oxidizing activities within biofilm, and thereby more corrosive compounds (e.g. sulfuric acid) were produced.

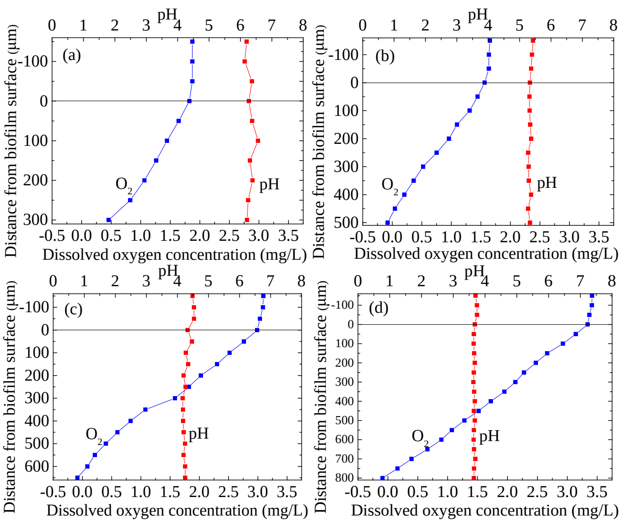

Fig. 8. Microelectrode test results of biofilms in sewage: a) BC1; b) BC2; c) BC3; d) BC4

3.3 Macroscopic performance of concrete in sewage

The performance of concrete in sewage was tested for 5 months. The concrete specimens immersed in sewage with COD concentrations of 300, 3000, 6000 and 9000 mg/L are designated as CC1, CC2, CC3 and CC4, respectively.

Corrosion morphology

After being immersed in the sewage for 5 months, the concrete specimens were washed and dried, and their appearance is shown in Fig. 9. It can be seen that the surface spalling of concrete was serious, moreover, the higher the sewage concentration was, and the more serious the concrete corrosion would be. For cube specimens in the intensified sewage, no prominent angularities can be observed, and the specimen CC4 almost showed a kind of ball shape. Obviously, concrete suffered more serious corrosion in the sewage with a high COD concentration.

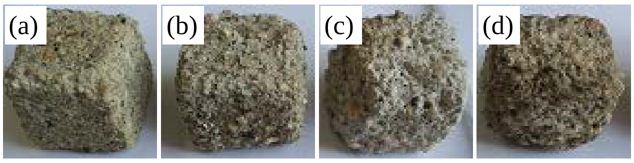

Fig. 9. Appearance of concrete specimens in sewage: a) CC1; b) CC2; c) CC3; d) CC4

Mass change

The weight of concrete specimens in water and sewage were tested once a month and the mass change can be obtained according to Eq. 1.

$$F_m = \left(\frac{M_a - M_b}{M_b} \right) \times 100\% \quad (1)$$

where F_m is the mass change of concrete (%); M_a is the mass of concrete after being immersed in sewage (g); M_b is the mass of concrete befor e being immersed in sewage (g).

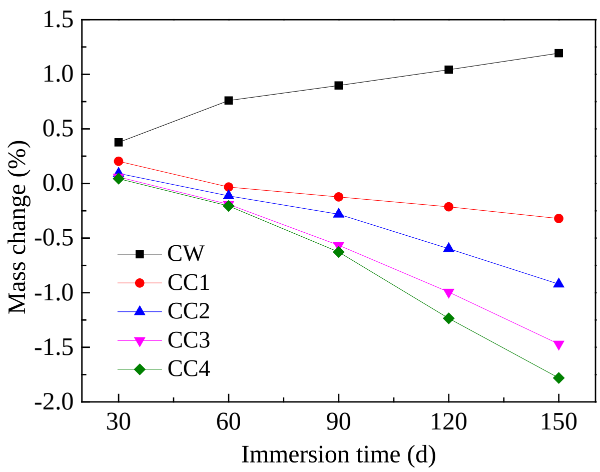

Fig. 10. Comparison of mass change of concrete specimens in water and sewage

From the results shown in Fig. 10, it can be seen that the mass change of specimens in clean water was positive value, indicating that the weight of specimens showed a tendency of rising with the time due to continuous water absorption. For the specimens immersed in sewage (CC1, CC2, CC3 and CC4), the mass change was also positive in the first month, whereas with the increase of corrosion time the weight of specimens decreased gradually, and after 150-day immersion the rates of decline were 0.32%, 0.92%, 1.47% and 1.78%, respectively. Obviously, the sewage with a high concentration can accelerate the concrete corrosion.

Compressive strength

After curing for 28 days, the initial strength of concrete specimens was tested, and the result is represented by one dotted line as shown in Fig. 11. Then the specimens were placed in water and sewage to make a comparative study. After a monthly test, the compressive strength of concrete specimens was obtained (Fig. 11) and it can be seen that the strength of specimens in water increased gradually due to the continuous hydration of cement particles. However, for the specimens in sewage, they also had small increases in compressive strength in the first month, which indicated that the cement clinkers can keep the hydration in sewage as well. After that, the concrete strength began to decrease compared with the initial value, and the drop kept increasing with the corrosion time. This was a sign of the deterioration of concrete microstructure. In the destructive test, the concrete in sewage showed less brittleness, which also indicated the destruction of concrete internal structure. Furthermore, the sewage with a high concentration can cause more serious corrosion. After 150 days of immersion, the strength of specimens CC1 and CC4 fell from 45.4 to 40.58 and 31.02 MPa, respectively. Therefore, the increase of COD concentration of sewage from 300 to 9000 mg/L led to the increase of decline rate of concrete strength from 10.6% to 31.7%. In other words, the sewage concentration increased by 30 times can triple the corrosion rate of concrete.

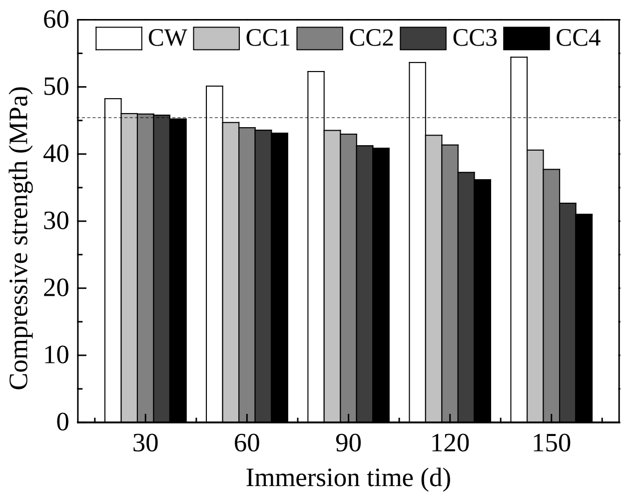

Fig. 11. Comparison of strength of concrete specimens in water and sewage

3.4 Microscopic performance of specimen in sewage

In order to further investigate the corrosion mechanism, the micro morphology, mineral compositions and pore structure of concrete specimens in water and sewage were studied.

SEM

After 90 days of immersion, the micro morphology of specimens was observed by SEM. Fig. 12(a) shows the SEM micrograph of a specimen in water, some flattened calcium hydroxide (CH) crystals, cluster like hydrated calcium silicate (CSH) gels and needle

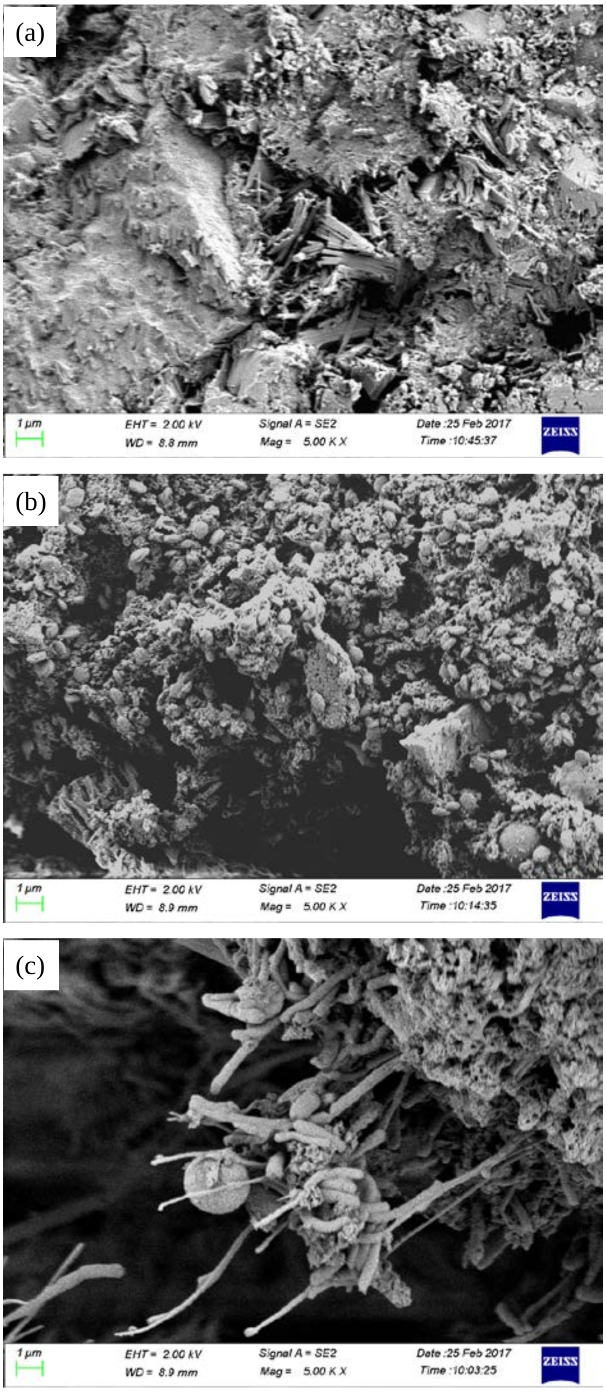

Fig. 12. SEM micrographs of concrete specimens in sewage: a) CW; b) CC2; c) CC4

shaped ettringite (AFt) crystals could be observed, and the closely packed products led to the formation of a relative dense structure. However, from the micrograph of specimens that immersed in sewage, it can be seen that the microstructure of cement paste became porous, and less CH crystal can be found. Moreover the CSH became loose and there was no gelling. Besides, on the surface of the hydration products, many egg-like and short rod-shaped microorganisms could be seen, as shown in Fig. 12(b) and (c). Obviously, the microstructure of cement paste had been damaged by sewage.

XRD

In order to further investigate the corrosion mechanism, the mineral compositions of the specimens were analyzed, and the results are shown in Fig. 13, it can be seen that the hydrate products for different cases were similar. They were mainly CH and some unhydrated clinker of C_3S and C_2S. However, the CH peak height of the specimens in sewage was significant lower than that of specimen in clean water. For specimens CC3 and CC4, the CH peak was barely noticeable, apart from some unhydrated clinkers, only some gypsum could be found in the hydrates. This result indicated the chemical reaction between CH and metabolic acid substance by microbes, and with the increase of sewage concentration, more corrosive compounds were produced.

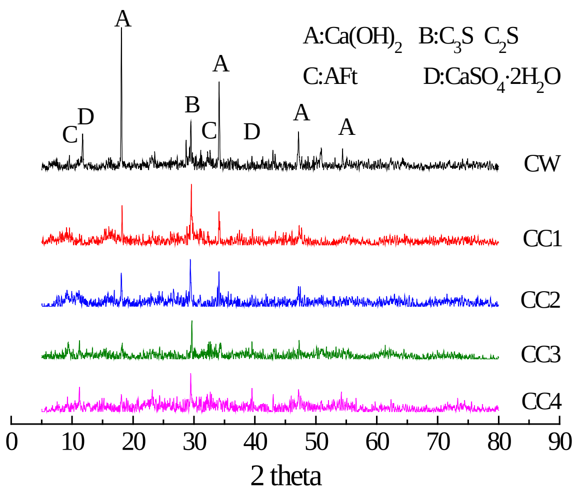

Fig. 13. XRD curves of the specimens in water and sewage

TGA

Heating the hardened cement paste, various hydration products can be decomposed or dehydrated at different temperature. By measuring the mass loss of the specific temperature stages, the content of the corresponding materials can be calculated. From the results of TGA as shown in Fig. 14(a), it can be seen that the weight loss of the cement paste samples between 50~400℃ (TG1), is mainly due to the dehydration of hydrated calcium silicates and ettringite, and that between 400~550℃ (TG2) and 550~770℃ (TG3), are caused by the dehydration of CH, and both the decomposition of the carbonization product and later dehydration of the hydrated calcium silicates and ettringite, respectively. Therefore, the CH content of the hydrates can be calculated as follows (Li, 2003):

$$M_1 = \left(\frac{TG_2}{18} + \frac{2}{3} \times \frac{TG_3}{44} \right) \times 74 \qquad (2)$$

where M_1 is the content of CH.

From Fig. 14(b) it can be seen that, the CH content of specimen in water (CW) was obviously higher than that of specimens in sewage, and with the increase of sewage concentration, the CH content decreased significantly. The CH content of specimen CC4 was only one third of that of CW. And with the increase of sewage COD concentration from 300 to 9000 mg/L, the CH content of specimen decreased from 12.6% to 5.3%. This was consistent with the XRD results.

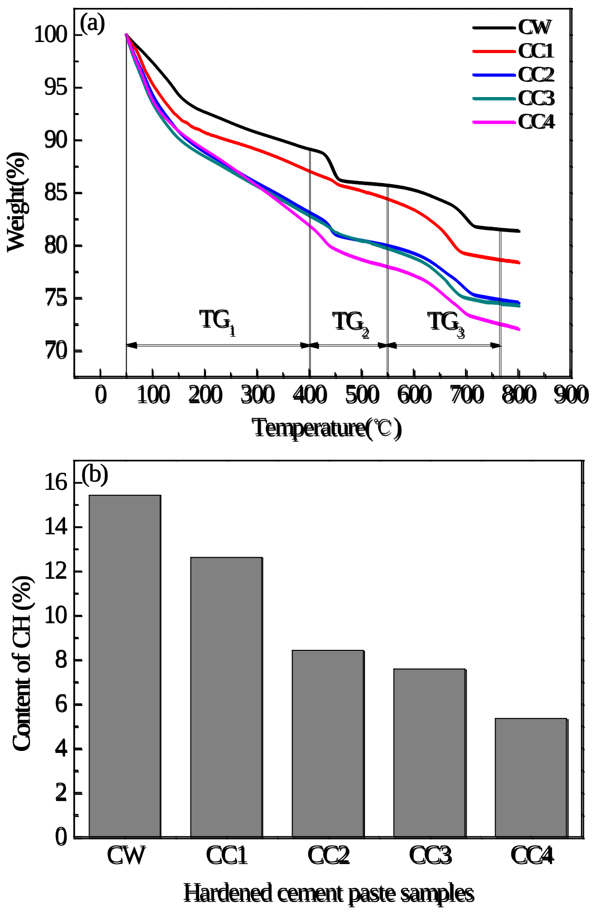

Fig. 14. Comparison of TGA of specimens in water and sewage: a) thermal-gravimetric curve; b) calcium hydroxide content

Pore structure

After 90 days of immersion, the pore structures of the surface specimens were also measured, and the cumulative intrusion of mercury into the specimens is shown in Fig. 15(a). It can be seen that the maximum mercury intrusion of specimens in sewage with different concentration were all significant higher than that of specimen in water. Moreover, with the increase of sewage concentration, the cumulative mercury quantity increased as well. In addition, the pores were divided into five parts: ＜10 nm, 10~100 nm, 100~1000 nm, 1000~10000 nm and ＞10000 nm. Among them, the pore in the range of 100~1000 nm and 1000~10000 nm belonged to medium and large capillary pores, which were detrimental to the durability of cement paste. Fig. 15(b) shows the pore size distribution of specimens in water and sewage. It is clearly that after 90-day water curing, the specimen in water had very little harmful pores, whereas the proportion of macropore that greater than 100 nm of specimens in sewage rose greatly, especially the specimens in the artificially intensified sewage (CC2, CC3 and CC4). Unlike the dense structure of specimens in water caused by the continuous hydration, the acidic substances produced by microbial metabolism in sewage had adverse effect on the microstructure of specimens.

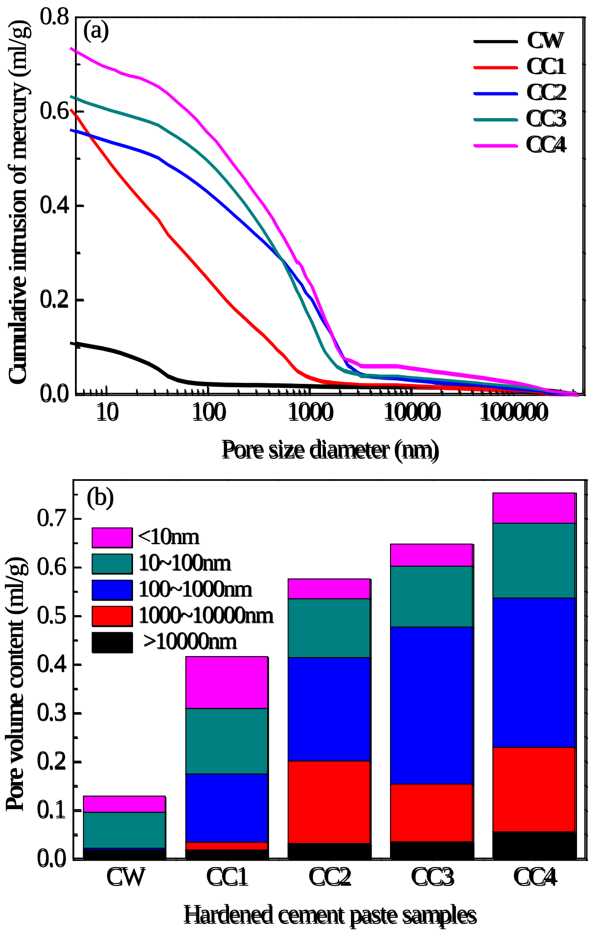

Fig. 15. Comparison of pore structure of specimens in water and sewage: a) cumulative mercury quantity curve; b) pore size distribution column

From the results shown in Table 2, it can be seen that the porosity of specimen in water had dropped from 29.70% to 20.55% after 90 days of immersion. In contrast, there were remarkable increases in the porosity of all the specimens in sewage. After 90 days corrosion, the porosity of the specimen CC4 almost doubled that of the specimen before corrosion, which presented the same trend that the intensified sewage made the microstructure of concrete more loose and porous.

Table 2. Porosity of specimens in water and sewage (%)

Before corrosion	After corrosion				
	CW	CC1	CC2	CC3	CC4
29.70	20.55	37.35	45.58	53.18	55.61

4.0 CONCLUSIONS

1. By taking the activated sludge as the parent and periodically adding right amounts of nutrients, the intensified sewage with high COD concentration can be prepared. A large amount of organic matter in sewage promoted the growth and reproduction of microorganisms, especially the dominant microorganisms (Bacteroidete, Proteobacteria, Firmicutes and Actiobacteria), which can produce some acids substance. Thereby, the increase of COD concentration of sewage from 300 to 9000 mg/L led to the decline of sewage pH from 6.4 to 2.3. It could be inferred that the artificially intensified sewage can be used as effective medium for accelerating the corrosion of concrete.

2. The biofilms developed on concrete specimens in artificial sewage was investigated by CLSM and microelectrode. The results show that with the increase of sewage concentration, the number of microorganisms and thickness of biofilm increased as well. Moreover, both the decline of pH level and O_2 concentration indicating that the large amounts of organic compounds and microorganisms in sewage with high concentration promoted the sulfate-reducing and sulfur-oxidizing activities within biofilm, and thereby more corrosive compounds were produced.

3. After being immersed in sewage for 150 days, evident spalling of surface mortar can be observed, and the cube specimens in sewage with high concentration almost had no prominent angularities and showed a kind of ball shape. The increase of COD concentration of sewage from 300 to 9000 mg/L led to the increase of mass loss of concrete from 0.32% to 1.78%, as well as the decline rate of concrete strength from 10.6% to 31.7%. That is, the sewage concentration increased by 30 times can triple the corrosion rate of concrete.

4. Over a period of 90 days, the microstructure of the specimens in sewage became loose and porous. From the XRD and TGA results it can be seen that the CH content of specimens in sewage was significant lower than that of specimens in clean water, which indicated the chemical reaction

between CH and some acid substance. And with the increase of sewage concentration, the CH content decreased significantly. Moreover, both the cumulative mercury quantity and harmful macropore proportion of specimens in intensified sewage were larger than that of specimens in water, and the porosity of specimens in sewage with a COD of 9000 mg/L was 55.61%, which was about two times of that of specimen before corrosion.

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