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Biogenic sulfuric acid corrosion resistance of new artificial reef concrete

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HIGHLIGHTS

- Biogenic sulfuric acid corrosion of concrete was studied.
- The effect of cement type on the performance of NARC was studied.
- Biogenic sulfuric acid corrosion of concrete was studied in a simulation device.
- Biogenic sulfuric acid corrosion resistance of NARC is superior to OPCC.

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ABSTRACT

Through biogenic sulfuric acid attack on concrete, comparisons between ordinary Portland cement concrete (OPCC) and new artificial reef concrete (NARC) prepared with sulphoaluminate cement, marine sand and sea water were made. Biogenic sulfuric acid corrosion resistance was studied by analyzing the surface and localized morphology, mass loss and compressive strength of both concrete specimens. The corrosion products were investigated by environmental scanning electron microscope (ESEM), X-ray diffraction (XRD) and Fourier-transform infrared (FT-IR). Results showed that the visually apparent corrosion degree and loss rates of mass and compressive strength are higher for OPCC than for NARC following exposure to biogenic sulfuric acid.

1. Introduction

Artificial reefs (AR) are submerged in seawater as a home for marine life. The material for AR varies widely, ranging from steel vessel and barge, natural rock and concrete block. Owing to low cost and ease of transportation and deployment, artificial reef concrete (ARC) has gained increasing attention. ARC is a suitable habitat for microorganisms, but the metabolic activities of microbes can cause serious corrosion on concrete [1,2]. The most typical microbial corrosion on concrete is the biogenic sulfuric acid corrosion [3]. The lower part of artificial reefs, which is generally constructed in shallow sea, is embedded in marine mud. In this habitat, sulfate-reducing bacteria convert rich sulfur-containing organic and inorganic materials into sulfide through biogenic metabolism [4]. Oxygen released during photosynthesis by nearby marine plants offers prerequisite conditions for sulfur oxidizing bacteria, such as Thiobacillus ferrooxidans, to oxidize sulfur compounds thereby generating biogenic sulfuric acid [5,6].

Previous research on sewer pipes under biogenic sulfuric acid attack has shown that the biogenic release of acid reacts with the cement hydration products in concrete, generating volume expanding gypsum and possibly ettringite. The relevant reactions are as following:

$$Ca(OH)_2\ (\text{portlandite}) + H_2SO_4 \rightarrow CaSO_4 + 2H_2O \tag{1}$$

$$3\ CaSO_4 \cdot 2\ H_2O\ (\text{gypsum}) + 3CaO \cdot Al_2O_3 + 26\ H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O(\text{ettingite}) \tag{2}$$

These expansive sulfate salts lead to internal cracks in the concrete and eventually to structural failure [7]. Previous studies have confirmed [8] that gypsum and ettringite are the main products of biogenic sulfuric acid corrosion. However, the differences lied in the generated order and the amount of the two corrosion products and their effects on the cement matrix. Some studies [8,9] found that the attack of biogenic sulfuric acid on concrete is more serious than that of chemical sulfuric acid. This is mainly attributed to the soft layer on concrete surface creating excellent conditions for the

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growth of the bacteria, which results in increased production of biogenic sulfuric acid. Microorganisms can penetrate inside the concrete matrix even if there are no observable cracks in concrete, the action of which increases concrete porosity [10]. The higher porosity in turn accelerates the biogenic sulfuric acid attack and thus exacerbates the deterioration of concrete substrate.

The chemistry of the cementitious material and aggregate within concrete is believed to impact on the rate of biogenic sulfuric acid induced corrosion. The use of high-alumina cements, calcareous aggregates and the inclusion of antimicrobial and silicates admixtures have shown varying degrees of success in slowing down the rate of corrosion [11–13]. Alexander and Fourie [11] reported that under biogenic sulfuric acid conditions in sewers, concrete containing calcium aluminate cement clearly outperformed ordinary Portland cement concrete (OPCC). This is ascribed to the ability of calcium aluminate cement to stifle the metabolism of the acid-generating bacteria, thereby reducing acid generation. Robin et al. [12] reported that the pores and integrity of the corrosion layer are determined by the concrete composition resulting in varying performance of different types of cement concrete when attacked by biogenic sulfuric acid. The transport of H^+ into the concrete is related to aggregate tortuosity, which is determined by the amount of aggregate and the gradation curves. Accordingly, the greater bulk density of aggregate leads to a smaller neutralization ability towards sulfuric acid in concrete.

In our previous work [14], a new artificial reef concrete (NARC) was fabricated with sulphoaluminate cement, marine sand and sea water. The experimental results showed that the workability (slump, slump loss cohesiveness and water retention) satisfied actual construction requirements and the mechanical properties (compressive strength, splitting tensile strength and dynamic elastic modulus) were better than OPCC. However, it was reported that there is little evidence showing that increased concrete strength or decreased permeability improves the resistance of biogenic sulfuric acid corrosion [15,16]. Additionally, it is imperative to explore the corrosion resistance of NARC when used under biogenic sulfuric acid conditions. In this context, the primary objective of this paper is therefore to provide preliminary understanding about the biogenic sulfuric acid corrosion resistance of NARC and the underlying mechanisms.

2. Experimental

2.1. Materials

A grade 42.5R Portland cement (Based on Chinese cement grading system, 42.5R cement can produce a fast-hardening cement mortar with a 28d compressive strength of 42.5 MPa.) and a grade 42.5R fast-hardening sulphoaluminate cement (Tangshan Polar Bear Building Materials Company, Hebei Province) were used for making OPCC and NARC, respectively. Chemical compositions of the two cements are listed in Table 1. The coarse aggregate used is ordinary crushed stone; its physical properties are listed in Table 2. Fine aggregate used include river sand and marine sand; their physical properties are listed in Table 3. Water used in OPCC was the tap water of the Fuzhou municipal area. Artificial sea water was prepared by simulating the contents of sea water per the mass proportions as shown in Table 4. A superplasticizer(SP) KDSP-1 (Polycarboxylate retarding type) with a water-reducing ratio of 25% and a retarder for sulphoaluminate cement, produced by Tianjin BASF Chemicals Co. Ltd. were also used. Acidithiobacillus ferrooxidans (T.f. bacterium), from Xiamen ocean institute, was used in the experiment. Specifically, 10% T.f. bacteria solution was inoculated with 9 K medium (a medium specially used for culturing T.f. bacterium [17]) as a medium erosion solution for simulating biogenic sulfuric acid corrosion. The compositions of 9 K cultured medium is shown in Table 5.

Table 2
Physical properties of coarse aggregate.

Apparent density (kg/m^3)	Bulk density (kg/m^3)	Porosity (%)	Water absorption (%)
2660	1532	42.4	0.2

2.2. Biogenic sulfuric acid corrosion device

The biogenic sulfuric acid corrosion simulation device is schematically shown in Fig. 1, which has been modified based on the one reported in literature [18]. H_2S is produced in part 1 while part 2 conducts the biogenic sulfuric acid corrosion. H_2S was produced by Na_2S (0.086 M) and HCl (0.042 M). Volumetric flow of Na_2S and HCl was kept at 1.4 ml/min while a certain oxygen input quantity of 30 ml/min was maintained in the medium. H_2S was transformed into biogenic sulfuric acid due to the T.f bacteria in the cultured medium [4,6]. pH change within the cultured medium is shown in Fig. 2. Laboratory temperature was kept at 25 ± 2 °C to ensure an identical test condition. A period of 14 days was used as a cycle in this experiment and the solution of cultured medium was adjusted every other cycle.

2.3. Sample preparation

In light of the requirements of NARC, C50 mix proportions of ARC shown in Table 6 were designed in accordance with the design method of OPC mix proportion [19]. Here, OPCC denotes concrete made of ordinary Portland cement, river sand and fresh water. NARC denotes concrete made of sulphoaluminate cement, marine sand and sea water. To prepare the concrete samples, the additive (SP and retarder) was dissolved first in the water. The cement, sand and crushed stone were mixed in a mixer for 1 min and then the additive solution was added and stirred thoroughly for 2 min. Afterwards, the mixtures were cast in prismatic moulds (100 mm × 100 mm × 100 mm) and were carefully compacted to minimize the amount of entrapped air. The samples were then covered by plastic film and curing under 20 ± 2°C and over 80% relative humidity for 24 h. All specimens were demoulded and cured in sea water at a constant room temperature (20 ± 2 °C) for 27 additional days. Then they were moved into a ventilating chamber for 2 more days before subjecting to corrosion test in the biogenic sulfate corrosion simulation device. The corrosion time mentioned in the following sections was recorded from the beginning of the corrosion test, namely 30 days after the concrete was cast.

Table 1
Chemical composition of sulphoaluminate cement (SAC) and ordinary Portland cement (OPC) (%).

Type	C_3S (tricalcium silicate)	C_2S (dicalcium silicate)	C_3A (tricalcium aluminate)	SO_3	C_4AF (tetracalcium alumino ferrite)	C_4A_3S (calcium sulpho aluminate)
OPC	55.6	19.6	7.5	2.1	9.3	–
SAC	–	31.4	–	2.9	11.2	52.8