



Study on corrosion mechanism of alkali-activated concrete with biogenic sulfuric acid

Yudong Xie, Xujian Lin*, Weijie Pan, Tao Ji, Yongning Liang, Hongru Zhang

College of Civil Engineering, Fuzhou University, Fuzhou, Fujian Province 350108, China

HIGHLIGHTS

- Biogenic sulfuric acid (BSA) corrosion of AAC was studied.
- The effect of sulfuric acid type on the performance of AAC was studied.
- The degradation mechanism of AAC eroded by BSA was analyzed.
- The BSA had a more negative effect on the performance of AAC.

ARTICLE INFO

Article history:

Received 7 May 2018

Received in revised form 12 August 2018

Accepted 17 August 2018

Keywords:

Biogenic sulfuric acid

Alkali-activated concrete

Deterioration

Corrosion

pH values

ABSTRACT

Two different types of sulfuric acid, chemical sulfuric acid (CSA) and biogenic sulfuric acid (BSA) produced by *T.f* bacteria (*Thiobacillus ferrooxidans*), were applied into the simulation of the corrosion of alkali-activated concrete (AAC). Compared with CSA corrosion, three sulfuric acid concentrations (pH = 1.1, 1.6 and 2.0) were used to study the degradation of AAC under the BSA corrosion. In this paper, the change of appearance, compressive strength, Ca^{2+} emission, the environmental scanning electron microscope-energy dispersive spectroscopy (ESEM-EDS), X-ray diffraction (XRD) and nuclear magnetic resonance (NMR) respectively were used to study the deterioration mechanism of AAC under BSA attack. The result of the experiment revealed that BSA was more corrosive to AAC than CSA. However, with the impact of different concentrations of CSA and BSA, the product of corrosion of the AAC was still mainly gypsum. Therefore, BSA merely accelerated the corrosion rate and did not transform the corrosion mechanism. Additionally, AAC less affected by bacteria, the degree of corrosion of the AAC is mainly influenced by the concentration of sulfuric acid.

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1. Introduction

Microbes producing sulfuric acid exert a negative influence on concrete materials [1]. Such corrosion damage often occurs in certain areas where are enriched with microorganisms, such as underground structure, sewage systems as well as wastewater treatment systems [2]. The percentage of corrosion due to microorganisms is 10–20% in the damage of German building materials and roughly 10% in American concrete sewage pipe [3,4]. It is imperative to study the microbial corrosion of concrete for reduction in the hefty cost of building maintenance.

Parker [5] has discovered that the biological sulfuric acid (BSA) corrosion is one of the main reasons accountable for the concrete corrosion. Sulfate and organic sulfur is turned into H_2S by SRB in

anaerobic environments, and then H_2S is oxidized into BSA by SOB in aerobic environments.

Alkali-activated concrete (AAC) has much more advantages in engineering than ordinary Portland concrete (OPC) such as acid resistance and impermeability [6]. Therefore, it is imaginable that the potentiality of AAC in marine application is huge [7].

Currently, compared to the studies about alkali-activated cement paste under BSA corrosion, research on the corrosion of AAC by BSA has been hardly conducted. Sun and Wu [8] immersed alkali-activated fly ash cement paste in various concentrations of H_2SO_4 solutions; as a result, slight damage on the surface was found when immersed in 0.05% H_2SO_4 for 6 months; when immersing specimens in a 3% H_2SO_4 solution for 1 week, the surface was damaged. And when alkali-activated slag (AAS) concrete was immersed in an acetic acid solution (pH = 4) for 6 months, the change of compressive strength was very small [9].

* Corresponding author.

E-mail address: xjlin@163.com (X. Lin).

There has been little research on the corrosion of AAC by BSA compared to studies about sewer pipe made by concrete under BSA corrosion [10,11]. It is improper to investigate the corrosion of concrete merely by chemical sulfuric acid (CSA) in that the process of BSA corrosion is a complex and long-term. Thus, the differences between BSA and CSA were of significance [12–15]. What's more, there is no study on the effect of BSA of different concentrations on the behavior of AAC. This paper studies the behavior of AAC under BSA with three different concentration levels. T.f bacteria (*Thiobacillus ferrooxidans*, T.f) was used to simulate the BSA corrosion in this paper. CSA was applied to study the corrosion effect of BSA on AAC as a contrast, which revealed the mechanism of AAC by BSA corrosion.

2. Materials

All materials used in the experiment were produced in China. The chemical composition of Fuzhou slag and fly ash is shown in Table 1. Analytical Reagent NaOH (the solid content is 96%) was used as activator. The coarse aggregate was ordinary stone, which was selected in accordance with GB/T 14685-2001 [16]; Fine aggregate was river sand, and its each performance index measured according to GB/T 14684-2001 [17] is listed in Table 2. Water used in AAC was the tap water of the Fuzhou municipal area. According to the Berger Bacteria Identification Manual [18], *Thiobacillus ferrooxidans* (T.f) from Xiamen Ocean Institute selected as the representative bacterium of ASOM was used in this study. Specifically, 10% T.f bacteria solution inoculated with 9 K medium (a medium specially used for culturing T.f bacterium [19]) was used as a medium erosion solution for simulating BSA corrosion. 9 K cultured medium contained 3 g $(\text{NH}_4)_2\text{SO}_4$, 0.1 g KCl, 0.5 g K_2HPO_4 , 0.5 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.01 g $\text{Ca}(\text{NO}_3)_2$, 44.78 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 1000 ml H_2O .

3. Experimental

3.1. Mix proportion

Because the superplasticizer is generally not suitable for AAC, and the current has not developed a water-reducing agent widely used for AAC. Thus, no water-reducing agent was added in this experiment.

Puertas et al. [20] reported that the ratio of fly ash-slag and the activator concentration always turn out to be critical factors. They have found that the mixture 50% fly ash-50% slag activated with 10 M NaOH solution develops compressive strength of 50 MPa. After repeated trial, the mixture 20% fly ash-80% slag by mass activated with 5.44 M NaOH solution was proportioned in this study, and the compressive strength at 28 days can reach 65.5 MPa. The final mix proportion is shown in Table 3.

Table 1
Chemical composition (% wt.).

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	TiO_2	Na_2O	LOI
Slag	32.85	13.01	0.29	37.44	10.78	1.91	2.15	0.32	0.2
Fly ash	50.02	24.96	4.46	7.52	1.47	1.06	1.57	0.78	4.01

Table 2
Performance index of the river sand.

Fineness modulus	Bulk density (kg/m^3)	Apparent density (kg/m^3)	Water absorption (%)	Mud content (%)
2.5	1480	2591	0.1	3.53

Table 3
Mix proportion of alkali-activated concrete (AAC) (kg/m^3).

Water	Slag	Fly ash	NaOH	Stone	River sand
170	369.19	92.30	38.51	1233	527

3.2. Specimen preparation

To prepare the concrete specimens, NaOH was dissolved first in the water to form a solution. The slag, fly ash, sand and crushed stone were mixed in a mixer for 1 min and then the NaOH solution was added and stirred thoroughly for 1 min. Afterwards, the mixtures were poured into inner surface-oiled moulds (100 mm \times 100 mm \times 100 mm) and were carefully compacted to minimize the amount of entrapped air. Then, the specimens were cured in a fog room (20 ± 2 °C, RH > 95%) for one day. The specimens were then demoulded from the moulds and were transferred into steam pressure equipment and then experienced an autoclaved curing (had a vacuum pumping for 30 min first, and then increased temperature to 195 °C and pressure to 1.2 MPa for 1 h, the temperature and pressure should be maintained for 6 h, and then reduced the pressure in 2 h). Subsequently, the specimens were cured in standard for 28 days. After that, the specimens were placed in the prepared CSA solution and BSA solution for corrosion test.

3.3. Biogenic sulfuric acid corrosion device

The BSA corrosion simulation device is schematically shown in Fig. 1, which has been performed as previously described in literature [21]. The experiment was carried out by changing the concentration of H_2S and keeping the other parameters unchanged so that obtained three different pH values (pH = 1.1, 1.6 and 2.0) of the bacterial broth in the course of the experiment to consider the effect of different bacterial growth conditions on the concrete specimen. The following is a brief description of the simulated BSA corrosion device, which is as follows:

H_2S is produced in part 1 while part 2 conducts the BSA 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 certain oxygen input quantity of 30 ml/min was maintained in the medium. H_2S was transformed into BSA due to the T.f bacteria in the cultured medium [22,23]. The change of pH 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.

In order to make a comparison of the CSA and BSA, the samples were placed in a simulated acid rain corrosion test chamber with CSA solution in the course of the experiment on CSA corrosion. Due to the large acid consumption of CSA during the test, the sul-

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