



Effect of electrical field on TSA failure of cement-based materials



Yaoling Luo, Chong Wang*, Chaoqun Luo, Qian Huang, Shupin Wang, Xiaoqin Peng

College of Materials Science and Engineering, Chongqing University, Chongqing 400045, China

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ABSTRACT

The impact of electrical field on the sulfate attack of cement-based materials at low temperatures was studied to rapidly detect Thaumasite Sulfate Attack (TSA) in the laboratory and in future engineering. Sulfate attack of cement paste with 30 wt% replacement of CaCO_3 powder soaked in Na_2SO_4 solution, MgSO_4 solution, or CaSO_4 solution was measured under the condition of $5 \pm 2^\circ\text{C}$ when an electrical field was applied. Appearance changes and compressive strength of the samples were tested to evaluate the corrosion degree. Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Raman Spectroscopic measurements were applied to study the microstructure of the corrosion product. The test results indicate that sample damage was obvious, compression strength declined rapidly, and ettringite and/or thaumasite were found in the corrosion product after applying the electrical field for 90 days. A muddy product with TSA characteristics was formed, and thaumasite composition was found in the corrosion product after applying the electrical field for 120 days when MgSO_4 solution was used as the corrosion medium. It is confirmed that an electrical field can accelerate TSA failure in cement-based materials.

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1. Introduction

The influence of electrical fields on concrete, e.g., the stray current produced by urban rail transit, has been gradually recognized in engineering. The traction of urban rail transit is DC power, and steel railing has significant resistance, leading to the potential difference in the steel rail and the potential difference between the steel rail and concrete roadbed. The electric current that transfers into the concrete is called stray current. These corrosion problems have been discovered in Beijing and Tianjin in China and in Japan and America [1]. Concrete structures can also be corroded by sulfate from the soil, groundwater, and seawater in these regions. Moreover, concrete can be influenced by electrical fields produced by the electro-osmosis pulse used for water-proofing and damp-proofing [2,3]. Electro-osmosis pulse has been successfully applied for water-proofing and damp-proofing of concrete; however, when sulfates are present in the soil and groundwater, concrete will be corroded by the electric field and sulfate attack. Nevertheless, scholars have focused on the electrochemical corrosion of reinforcement in concrete [4–7] by electrical fields, ignoring the influence of electricity on cement. In particular, concrete is more easily corroded in cold regions, producing thaumasite [8,9]. Therefore, concrete is subject to more serious damage in the presence of an electrical field.

The durability of concrete may degrade through use for internal and external reasons, which has economic consequences for countries. Moreover, this degradation also increases potential risk [10]. Sulfate attack to concrete is the most sophisticated type of corrosion. Sulfate from soil and ground water can react with the cement, which results in the expansion, cracking and spalling of concrete [11]. Thaumasite Sulfate Attack (TSA) is one corrosion mechanism of sulfate attack that was discovered in recent decades and has attracted increasing attention from researchers [12–14]. TSA is a special form of corrosion of cement-based materials that occurs naturally in minerals of the type $\text{CaSiO}_3 \cdot \text{CaSO}_4 \cdot \text{CaCO}_3 \cdot 15\text{H}_2\text{O}$ and has been found in metamorphosed rocks that have undergone hydrothermal changes over time. Thaumasite is a pulp without bonding capabilities that contributes to the destruction of concrete construction [15,16]. The formation rate of thaumasite is usually decades in nature [17]. However, thaumasite can be rapidly produced within 6 months to 2 years in the laboratory by soaking in magnesium sulfate solution or inner-introduced sulfate at low temperatures [18,19]. The long period required to form thaumasite is a disadvantage in the laboratory and in some real-world detection tests. Therefore, it is necessary to research the sulfate attack of cement-based materials under electrical field conditions, which can not only accelerate the study of TSA as a method for testing quickly TSA in laboratory, but can also provide insight into the deterioration mechanism of concrete exposed to an electrical field and sulfate in engineering.

The aim of this paper is to study the acceleration rates of three types of sulfates (Na_2SO_4 solution, MgSO_4 solution and CaSO_4 solution) under

* Corresponding author.

E-mail addresses: 504360595@qq.com (Y. Luo), chongwang@cqu.edu.cn (C. Wang).

an electrical field and the mechanism of sulfate and electrical corrosion of cement-based materials.

2. Materials and methods

2.1. Preparation of basic materials

Grade 42.5R of ordinary Portland cement composed with 97wt% clinker and 3wt% dihydrate gypsum were prepared. The chemical components of the cement clinker are listed in Table 1. Limestone powder with $\text{CaCO}_3 \geq 98$ wt% was obtained from Bao Xing Company, Sichuan province China. The XRD of the cement clinker and limestone powder are presented in Fig. 1 and Fig. 2.

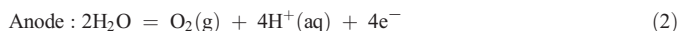
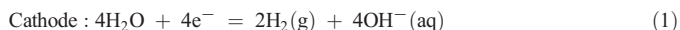
2.2. Specimen preparation

Cement paste was prepared to test thaumasite formation via the action of an electrical field. The mixture proportions are listed in Table 2.

The fresh paste was casted into a PMMA mould with three cube specimens with dimensions of 40 mm × 40 mm × 40 mm, which have two end containers for the sulfate solution. The specimens, together with the mould, were cured for 28 days in a moist room at a temperature of $(20 \pm 2)^\circ\text{C}$ with a relative humidity of no less than 95% until testing. After curing, the specimens, together with the mould, were moved into a refrigerating cabinet with a temperature of $5 \pm 2^\circ\text{C}$ (shown in Fig. 3 [20] and Fig. 4). Two titanium alloy staffs were used as the anode and cathode materials, respectively. An electrical field was applied to accelerate the migration of sulfate ions into the cement-based materials. The electrical voltage was 30 V, and the period was 20 s. The waveform of electrical pulses is shown in Fig. 5 [20].

All cathode solutions were Na_2SO_4 solutions. The anode solutions were Na_2SO_4 solution (EFN), MgSO_4 solution (EFM), and CaSO_4 solution (EFC). The control group consisted of samples fully immersed in MgSO_4 solution (M); the SO_4^{2-} concentration of the four groups of sulfate solutions was 0.38 mol/l, and the solution was replaced every 7 days. Samples fully immersed in MgSO_4 solution were denoted as the control group because MgSO_4 can promote thaumasite sulfate attack of cement-based materials. The research results of Hobbs DW [21] showed that magnesium ions and the formation of insoluble $\text{Mg}(\text{OH})_2$ can reduce the pH and increase the degree of chemical attack on C–S–H, thus playing a major role in increasing the occurrence of thaumasite attack. The acceleration of thaumasite formation (TF) in MgSO_4 solution was also confirmed by Zangun Liu [22]. Moreover, additional studies [23,24] have used MgSO_4 solution to research the thaumasite sulfate attack of cement-based materials.

According to the principle of electrochemistry, water was electrolyzed on the electrode and electrolysis cannot happen within the cement sample. The process of water electrolysis is as follows:



The corrosion liquid of the cathode is basic, and the corrosion liquid of the anode is acidic under an electrical field. Moreover, the anion will

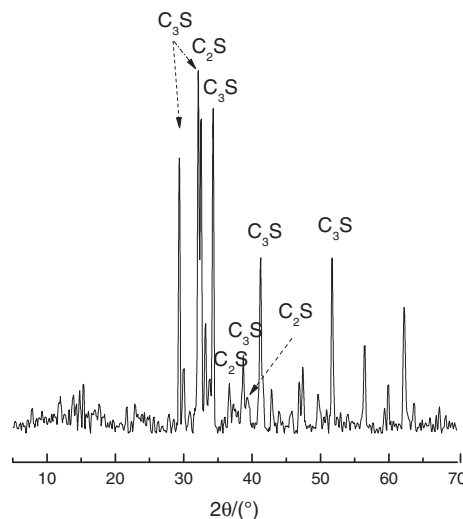


Fig. 1. XRD of cement clinker.

migrate from the cathode to the anode under the action of an electrical field. Therefore, SO_4^{2-} migrates from the cathode to the anode, leading to the accumulation of SO_4^{2-} on the cathode side of the sample [20, 25–28]. The sulfate attack of cement usually occurs in an alkaline environment, and the abundance of SO_4^{2-} in the cathode leads to the acceleration of TSA in the cathode, while mainly ionic migration and acid corrosion occur in the anode.

These samples were observed every 30 days, and the damage grades were judged according to Table 3 [24] until failure character of TSA was occurred in these samples. Then, micro samples were created for XRD, SEM, and EDS tests. FTIR was used to identify the microstructure of thaumasite formation. The samples for the analysis of thaumasite formation were produced by taking small pieces from the cathode side of the attacked specimen. The broken pieces were soaked and rinsed using anhydrous alcohol and oven dried at 50°C . The X-ray diffractometer used was from Ricoh Company with D/MAX-IIIC and $\text{CoK}\alpha$ radiation ($0.2 \text{ \AA}$). VEGA II SEM instrument with EDS was from Tescan Company. The SEM investigation was carried out using an accelerating voltage of 20 kV. Fourier Transform Infrared Spectroscopy (FTIR) instrument with a resolution of 4 was used. Raman spectroscopic measurements were carried out using a HORIBA Jobin Yvon S.A.S. spectrometer (product model: LabRAM HR Evolution; spectral resolution: visible spectral $\leq 0.65 \text{ cm}^{-1}$; spectral region from 200 nm to 1050 nm).

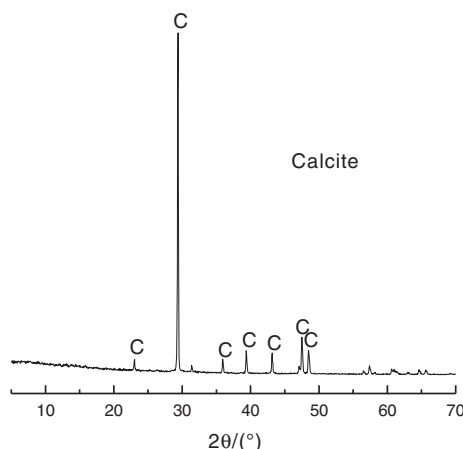


Fig. 2. XRD of limestone powder.

Table 1
Chemical components of clinker, dihydrate gypsum, and limestone powder (wt%).

Materials	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	LOI
Clinker	19.99	2.98	4.80	61.22	3.27	0.23	0.88	0.18	3.52
Gypsum	4.47	0.36	0.99	34.05	1.84	40.61	0.23	0.08	16.87
Limestone powder	0.23	0.21	–	55.46	–	–	–	–	41.75

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